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„Extraktion quantifizierbarer Information aus komplexen Systemen”

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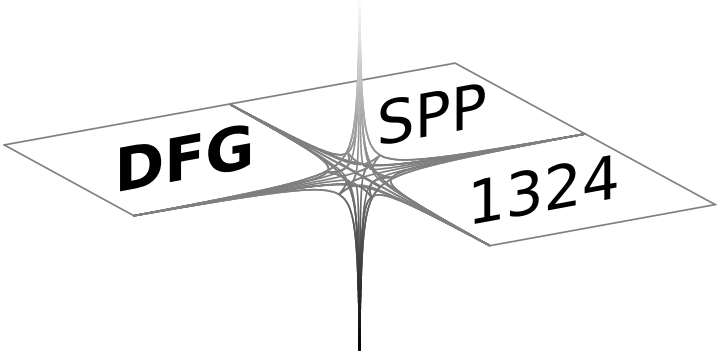
H. Chen, R. Schneider

Preprint 116



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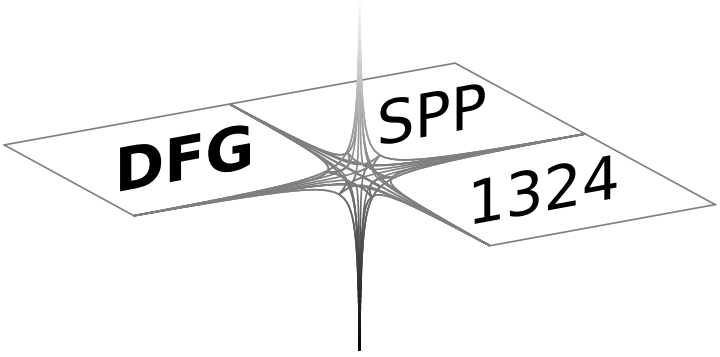

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Numerical analysis of augmented plane waves methods for full-potential electronic structure calculations

Huajie Chen *and Reinhold Schneider †

Abstract

This paper analyze the augmented plane wave methods which are widely used in full-potential electronic structure calculations. These methods introduce a bases set that describe different regions using different discretization schemes. We construct a nonconforming method based on this idea and present a systematic a priori error estimate for both linear Schrödinger type equations and nonlinear Kohn-Sham equations. Some numerical experiments are presented to support our theory.

1 Introduction

Electronic structure theory describes the energies and distributions of electrons, which is essential in characterizing the microscopic structures of molecules and materials in condensed phases. Among all the different formalisms, Kohn-Sham (KS) density functional theory (DFT) [36] achieves so far the best compromise between accuracy and efficiency when dealing with extended systems, in particular periodic bulk crystals.

For a system composed of M nuclei (located at $\mathbf{R}_k \in \mathbb{R}^3$ with charge $Z_k \in \mathbb{Z}_+$, $k = 1, \cdots, M$) and N electrons, KS-DFT gives rise to the following KS equations

$$H_\Phi \phi_i = \lambda_i \phi_i, \quad \lambda_1 \leq \lambda_2 \leq \cdots \leq \lambda_N, \tag{1.1}$$

where $\Phi = \{\phi_1, \cdots, \phi_N\}$ and the Hamiltonian H_Φ is given by

$$H_\Phi = -\frac{1}{2}\Delta + v_{ext} + v_H(\rho_\Phi) + v_{xc}(\rho_\Phi) \tag{1.2}$$

with the external Coulomb potential $v_{ext}(\mathbf{r}) = -\sum_{k=1}^{M} \frac{Z_k}{|\mathbf{r} - \mathbf{R}_k|}$, the Hartree potential $v_H(\rho_\Phi) = \int_{\mathbb{R}^3} \frac{\rho_\Phi(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$, the exchange-correction potential $v_{xc}(\rho_\Phi)$ and the electron density $\rho_\Phi(\mathbf{r}) =$

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$\sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2$. A self-consistent field iteration (SCF) algorithm are commonly resorted to for these nonlinear problems. In each iteration of the algorithm, a Hamiltonian $H_{\tilde{\Phi}}$ is constructed from a trial electronic state $\tilde{\Phi}$, and a linear eigenvalue problem is then solved to obtain the low-lying eigenfunctions.

In studies of the electronic structure of periodic solids, plane waves are natural bases corresponding to Bloch functions labeled by the k-vector of the first Brillouin zone. The pseudopotential approximations which replace the singular potential of nuclei and core electrons by a smooth potential are necessary to implement the plane wave methods. Although the pseudopotentials give satisfactory results in most cases but sometimes fails, and to our best knowledge, a mathematical analysis of the pseudopotential approximation is still lacking. Moreover, the core electrons have to be considered sometimes and are responsible for many properties. Therefore, the full-potential/all-electron calculation is necessary, while plane waves are not efficient bases for describing the cusp [23, 26] and the rapidly varying wave functions close to the nuclei.

In order to overcome the difficulties in full-potential calculations, one can augment the plane waves bases set as done in the augmented plane wave (APW) method [36, 40], which is among the most accurate methods for performing electronic structure calculations for crystals. The APW method is originally proposed by Slater [44] in 1937, in spite of demanding computational cost due to the energy dependency, it has been widely and successfully used, e.g., [19]. Several improvements of the bases set were tried to get rid of the energy dependency, the first really successful one was the linearization scheme introduced by Andersen [4] in 1975, leading to the linearized augmented plane wave (LAPW) method [33]. The method is further developed recently by including local atomic orbitals (APW+lo) to have enough variational flexibility in the radial bases functions [35, 42, 43]. Several widely used quantum chemistry and solid-state physics softwares are based on these methods such as Exciting, FLEUR, and WIEN2k.

In APW method, the unit cell Ω is partitioned into two types of regions (the so-called "muffin-tin" division [36], see Figure 1): (i) spheres $\mathscr{C}_i$ centered around atomic sites $\mathbf{R}_i$ with a radius R_i, (ii) the remaining interstitial region $\mathscr{D}$. The augmented bases then consist of augmentation of plane waves as follows

$$|\Omega|^{-\frac{1}{2}} e^{i\mathbf{k}\cdot\mathbf{r}} \;\rightarrow\; \begin{cases} |\Omega|^{-\frac{1}{2}} e^{i\mathbf{k}\cdot\mathbf{r}} & \text{in } \mathscr{D}, \\ \displaystyle\sum_{lm}^{L} \alpha_{lm}^{\mathbf{k}} \chi_l(r,\varepsilon) \tilde{Y}_{lm}(\mathbf{r}) & \text{in } \mathscr{C}_i, \end{cases} \tag{1.3}$$

where $r = |\mathbf{r} - \mathbf{R}_i|$, $\tilde{Y}_{lm}(\mathbf{r})$ denotes the spherical harmonic functions[1], $\chi_l(r,\varepsilon)$ is the solution of the radial Schrödinger equation at energy parameter ε

$$-\frac{1}{2r^2}\frac{d}{dr}\left(r^2\frac{d\chi_l}{dr}\right) + \left(\frac{l(l+1)}{2r^2} + V(r) - \varepsilon\right)\chi_l = 0, \tag{1.4}$$

and the coefficients $\alpha_{lm}^{\mathbf{k}}$s are chosen such that atomic functions for the lth component match the plane waves at the spherical surface. The philosophy of APW method is a procedure for

[1]Using polar coordinates $\mathbf{r} \rightarrow (r,\theta,\phi)$, we express $\tilde{Y}_{lm}(\mathbf{r}) = Y_{lm}(\theta,\phi)$, where $Y_{lm}(\theta,\phi)$ is the spherical harmonics on S^2. This notation will be used throughout this paper.

solving the KS equations for the ground states of a many electron system by introducing a bases set that is in some ways the "best of both worlds". The smoothly varying parts of the wavefunctions between the atoms are represented by plane waves, and the rapidly varying parts near the nuclei are represented as radial atomic functions time spherical harmonics inside a sphere around each nucleus.

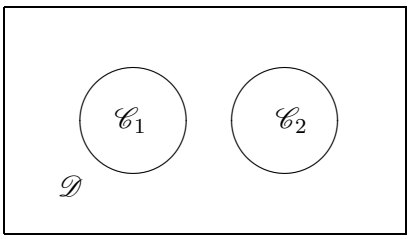

Figure 1.1: The "muffin-tin" division of the unit cell Ω into spheres $\mathscr{C}_i$ centered at atoms and interstitial region $\mathscr{D}$.

The purpose of this paper is to construct a discretization method based on the idea of the augmented methods and provide a numerical analysis for full-potential periodic electronic structure calculations. As far as we know, there is no numerical analysis concerning the augmented methods in literature. We shall first consider linear Schrödinger type eigenvalue problems with an effective potential, which appear in each step of the self consistent cycle. Afterwards we extend the analysis to the nonlinear KS equations under certain reasonable coercive assumptions.

Standard plane waves and finite element methods for numerically solving (1.1) are based on variational principles, which consist in constructing a finite dimensional subspace of the Sobolev space $H^1(\Omega)$. Such conforming methods have been extensively studied for linear problems and convergence results are classical (see, e.g. [5, 13]). In contrast, the APW bases $\chi_{\mathbf{k}}$ are not continuous on the spherical surface due to the truncation of L to get the coefficients $\alpha_{lm}^{\mathbf{k}}$ in (1.3), so the finite dimensional approximation space is no longer contained in $H^1(\Omega)$. Therefore, one gets a nonconforming method by APW bases. There are a lot of existing works on analysis of the nonconforming finite element methods for solving linear second order elliptic problems, see e.g. [16, 28, 32, 45]. The advantages of the nonconforming idea in augmented methods lie in: (i) coupling different variational discretizations so as to take profit of the efficiency of each of them; (ii) more flexible and economical adaptive procedures as the nonconformity results assuredly in limiting the contamination only to the subdomain where refinement is needed. The nonconforming ideas in augmented methods are also highly related to the mortar methods which match incompatible grids with a suitable variational operator ensuring an optimal transmission of information between adjacent subdomains (see, e.g., [7, 8, 9]).

The KS equations form a nonlinear integro-differential eigenvalue problem with multiple eigenvalues to be considered, for which the numerical analysis is a difficult task. Let us remark that in general, like for the Hartree Fock equations, the energy functional of KS equations is neither convex nor concave. To our best knowledge, there are only a handful of very recent works concerning this problem, see, Cancès et al [12], Chen et al [14] and Suryanarayana et al [46], and none of these numerical analysis can be applied to the augmented bases. We shall

establish the convergence of the eigenpair approximations and obtain a priori error estimate, using the techniques that are related to the arguments in the work [12, 14, 30]. All the results in this paper deal with a priori analysis, while the results about a posteriori error analysis are even more difficult and shall be investigated in our future works.

An outline of this paper is as follows. In Section 2, we state the model problem and basic regularity results. In Section 3, we focus on linear eigenvalue problems. A nonconforming method analogous to APW methods, in particular LAPW, with a complete bases set is constructed and a priori error estimate is proved. Further, the (L)APW methods are investigated under this framework and a numerical analyss is given. In Section 4, we derive the a priori error estimates for ground state solutions of the nonlinear KS equations using the nonconforming methods constructed before. In Section 5, we present several numerical experiments to support our theoretical analysis. Finally, some concluding remarks are made in Section 6.

2 Preliminary

Throughout this paper, we shall use C to denote a generic positive constant which may stand for different values at its different occurrences and is independent of finite dimensional subspaces. For convenience, the symbol $\lesssim$ will be used. The notation $A \lesssim B$ means that $A \leq CB$ for some constant C that is independent of the discretization parameters.

We consider $\Omega \in \mathbb{R}^3$ the simulation domain with periodic boundary conditions, by $\mathcal{R}$ the periodic lattice, and by $\mathcal{R}^*$ the dual lattice. For simplicity, we assume that $\Omega = [-\frac{L}{2}, \frac{L}{2}]^3$ ($L > 0$), in which case $\mathcal{R}$ is the cubic lattice $L\mathbb{Z}^3$, and $\mathcal{R}^* = \frac{2\pi}{L}\mathbb{Z}^3$. For $\mathbf{k} \in \mathcal{R}^*$, we denote by $e_{\mathbf{k}}(\mathbf{r}) = |\Omega|^{-1/2} e^{-i\mathbf{k}\cdot\mathbf{r}}$ the plane wave with wave vector k. The family $\{e_{\mathbf{k}}\}_{\mathbf{k}\in\mathcal{R}^*}$ forms an orthogonormal bases of

$$L^2_{\#}(\Omega) = \{u \in L^2_{loc}(\mathbb{R}^3) \ : \ u \text{ is } \mathcal{R}-\text{periodic}\}.$$

For all $u \in L^2_{\#}(\Omega)$, we have

$$u(\mathbf{r}) = \sum_{\mathbf{k}\in\mathcal{R}^*} \hat{u}_{\mathbf{k}} e_{\mathbf{k}}(\mathbf{r}) \quad \text{with} \quad \hat{u}_{\mathbf{k}} = (u, e_{\mathbf{k}})_{L^2_{\#}(\Omega)} = |\Omega|^{-1/2} \int_\Omega u(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}.$$

We introduce the Sobolev spaces of $\mathcal{R}$-periodic functions

$$H^s_{\#}(\Omega) = \left\{ u(\mathbf{r}) = \sum_{\mathbf{k}\in\mathcal{R}^*} \hat{u}_{\mathbf{k}} e_{\mathbf{k}}(\mathbf{r}) \ : \ \sum_{\mathbf{k}\in\mathcal{R}^*} (1+|k|^2)^s |\hat{u}_{\mathbf{k}}|^2 < \infty \right\},$$

where $s \in \mathbb{R}$ and $k = |\mathbf{k}|$. For $K \in \mathbb{N}$, we denote the finite dimensional space by

$$\mathcal{V}_K = \left\{ v_K(\mathbf{r}) = \sum_{\mathbf{k}\in\mathcal{R}^*, |\mathbf{k}|\leq \frac{2\pi}{L}K} c_{\mathbf{k}} e_{\mathbf{k}}(\mathbf{r}) \right\}.$$

For all $s \in \mathbb{R}$ and each $v \in H^s_{\#}(\Omega)$, the best approximation of v in $\mathcal{V}_K$ for H^r-norm ($r \leq s$) is $\Pi_K v = \sum_{\mathbf{k}\in\mathcal{R}^*, |\mathbf{k}|\leq \frac{2\pi}{L}K} \hat{u}_{\mathbf{k}} e_{\mathbf{k}}(\mathbf{r})$. The more regular of v, the faster the convergence of this

truncated series to v: for real numbers r and s with $r < s$, we have

$$\|v - \Pi_K v\|_{H^r_\#(\Omega)} = \min_{v_K \in \mathcal{V}_K} \|v - v_K\|_{H^r_\#(\Omega)} \lesssim K^{r-s} \|v\|_{H^s_\#(\Omega)} \quad \forall\ v \in H^s_\#(\Omega). \tag{2.1}$$

As a model problem, we consider the following Schrödinger type linear eigenvalue problem, which can be viewed as a linearization of (1.1): Find $\lambda \in \mathbb{R}$ and $0 \neq u \in H^1_\#(\Omega)$ such that $\|u\|_{L^2(\Omega)=1}$ and

$$a(u, v) = \lambda(u, v) \quad \forall\ v \in H^1_\#(\Omega), \tag{2.2}$$

where the bilinear form $a : H^1_\#(\Omega) \times H^1_\#(\Omega) \to \mathbb{R}$ is defined by

$$a(u, v) = \frac{1}{2} \int_\Omega \nabla u \cdot \nabla v + \int_\Omega V_{eff} uv \tag{2.3}$$

with the effective potential V_{eff} being a smooth potential expect the singular points at the positions of nuclei.

For sake of simplicity, we shall restrict our discussions to a single nucleus located at origin, the algorithms and analysis of which can be easily generalized to multi-nuclei system problems. We denote afterwards that $\mathscr{C}$ is an sphere centered at the origin with radius R and spherical surface Γ.

It was shown in [21, 22, 23] that the exact electron densities are analytic away from the nuclei and satisfy certain cusp conditions at the nuclei. Note that the plane wave approximations cannot have as good convergence rate as (2.1) due to the cusp at the nuclear positions. In our analysis, we rely on the high regularity results in weighted Sobolev space for Schrödinger type eigenvalue problems developed by Flad, Schneider and Schulze [20], which provides asymptotic regularity of eigenfunctions to equation (2.2). This type of analysis has been introduced to investigate singularities for boundary value problems in conical domains with corners and edges, we refer to [6, 18, 25] for more details. In our case the geometry is fairly simple, while the Coulomb potential fits perfectly in this treatment.

Let $\mathfrak{p} \in L^2_\#(\Omega)$ be a continuous function such that $\mathfrak{p}(\mathbf{r}) = |\mathbf{r}|$ in the neighborhood of 0 and $\mathfrak{p} \in C^\infty_{\mathrm{loc}}(\mathbb{R}^3)$. We define the sth weighted Sobolev space with index γ of periodic functions by

$$\mathcal{K}^{s,\gamma}(\Omega) = \left\{ u \in L^2_\#(\Omega) \ :\ \mathfrak{p}^{\alpha-\gamma} \partial^\alpha u \in L^2_\#(\Omega) \ \ \forall\ |\alpha| \leq s \right\}. \tag{2.4}$$

Note that the difference between Sobolev space and the weighted Sobolev space is only the appearance of the weight function $\mathfrak{p}^{\alpha-\gamma}$. Next we consider the subspace of $\mathcal{K}^{s,\gamma}(\Omega)$ of certain asymptotic type using polar coordinates. These subspaces consist of functions with asymptotic expansions[2] as $r \to 0$

$$\breve{u}(r, \theta, \phi) \sim \sum_j \sum_{k=0}^{m_j} c_{jk}(\theta, \phi) r^{-p_j} \ln^k r, \tag{2.5}$$

[2]For a function $u(\mathbf{r})$, we denote by $\breve{u}(r, \theta, \phi)$ the polar coordinate representations, i.e., $u(\mathbf{r}) = \breve{u}(r, \theta, \phi)$. This notation will be used throughout this paper.

where c_{jk} belong to finite dimensional subspaces $L_j \subset C^\infty(S^2)$ and p_j are taken from a strip of complex plane with a finite number, i.e.,

$$p_j \in \{z : \frac{3}{2} - \gamma + \vartheta < \mathrm{Re} z < \frac{3}{2} - \gamma\}.$$

The asymptotic expansion (2.5) is completely characterized by the asymptotic type $P = \{(p_j, m_j, L_j)\}_{j\in\mathbb{Z}_+}$. Together, the weight data γ, ϑ and the asymptotic type P define the weighted Sobolev spaces with asymptotic

$$\mathcal{K}_P^{s,\gamma}(\Omega) = \left\{ u \in \mathcal{K}^{s,\gamma}(\Omega) \ : \ \breve{u}(r,\theta,\phi) - \omega(r) \sum_j \sum_{k=0}^{m_j} c_{jk}(\theta,\phi) r^{-p_j} \ln^k r \in \bigcap_{\varepsilon>0} \mathcal{K}^{s,\gamma-\vartheta-\varepsilon}(\Omega) \right\} \quad (2.6)$$

with $-\infty \le \vartheta < 0$ and $\omega(r)$ the cut-off function, i.e. $\omega = 1$ near 0 and $\omega = 0$ outside some neighborhood of 0. Space (2.6) is a Fréchet space equipped with the natural quasi-norms $\|\cdot\|_{\mathcal{K}_P^{s,\gamma}(\Omega)}$, we refer to [18] for further details.

Definition 2.1. *A function u is called asymptotically well behaved if*

$$u \in \mathcal{K}_P^{\infty,\gamma}(\Omega) \qquad \text{for} \quad \gamma < 3/2 \quad \textit{and} \quad P = \{(-j, 0, L_j)\}_{j\in\mathbb{Z}_+}. \quad (2.7)$$

The finite dimensional spaces $L_j \subset C^\infty(S^2)$ are given by $L_j = \mathrm{span}\{Y_{lm}, l \le j\}$.

We shall make the following assumption of the effective potential throughout this paper that

$$V_{eff}(\mathbf{r}) = -\frac{Z}{|\mathbf{r}|} + \rho * \frac{1}{|\mathbf{r}|} + v_s(\mathbf{r}) \quad \text{with} \quad v_s \in C_\#^\infty(\Omega), \quad (2.8)$$

where ρ is an asymptotically well behaved function and

$$C_\#^\infty(\Omega) = \{v \in C_{\mathrm{loc}}^\infty(\mathbb{R}^3) \ : \ v \text{ is } \mathcal{R}-\text{periodic}\}.$$

The following lemma concerning the regularity of the eigenfunctions of (2.2) is heavily used in our analysis, the proof of which can be referred to [20, Theorem 1,4 and Proposition 1].

Lemma 2.1. *The eigenfunction u of (2.2) is asymptotically well behaved.*

Lemma 2.2. *For any $s \in \mathbb{Z}^+$, there exists $\hat{s} \in \mathbb{Z}^+$ such that*

$$u \in \mathcal{K}_P^{\hat{s},\gamma}(\mathscr{C}) \qquad \text{for} \quad \gamma < 3/2 \quad \textit{and} \quad P = \{(-j, 0, L_j)\}_{j\in\mathbb{Z}_+}$$

with the finite dimensional spaces $L_j \subset C^\infty(S^2)$ given by $L_j = \mathrm{span}\{Y_{lm}, l \le j\}$ implies

$$u \in H^s([0, R] \times S^2).$$

Proof. For $s \in \mathbb{Z}_+$, we take $\hat{s} > s + \frac{3}{2}$, and express the function $u \in \mathcal{K}_P^{\hat{s},\gamma}(\mathscr{C})$ as

$$\breve{u}(r,\theta,\phi) = \omega(r)\sum_{j=0}^{k} r^j \alpha_j(\theta,\phi) + \Phi_{k+1}(r,\theta,\phi), \tag{2.9}$$

where $\Phi_{k+1} \in \mathcal{K}^{\hat{s},\gamma}(\mathscr{C})$ for $\gamma < \frac{5}{2} + k$. For sufficiently large k, $\Phi_{k+1} \in \mathcal{K}^{\hat{s},\hat{s}}(\mathscr{C})$, which according to the definition (2.4) is equivalent to

$$\sum_{|\alpha|<\hat{s}} \int_{[0,R]\times S^2} \mathbb{p}^{2|\alpha|-2s} |\partial^\alpha \Phi_{k+1}|^2 < \infty.$$

This implies $\Phi_{k+1} \in H^{\hat{s}}(\mathscr{C})$. According to Sobolev's lemma, we have $H^{\hat{s}}(\mathscr{C}) \subset C^s(\mathscr{C})$ for $s < \hat{s} - 2$, and hence $\Phi_{k+1} \in H^s([0,R]\times S^2)$.

Note that the first part of (2.9) already belongs to $C^\infty([0,R]\times S^2)$, we obtain $u \in H^s([0,R]\times S^2)$ and completes the proof. □

The following lemma will be used in our analysis, which states the relationship between two Sobolev norms.

Lemma 2.3. *If $v \in H^1(\mathcal{C})$, then there exits a constant C such that*

$$\|v\|_{H^1(\mathscr{C})} \le C\|v\|_{H^1([0,R]\times S^2)}.$$

Proof. Note that $v \in H^1(\mathcal{C})$ implies

$$\lim_{r\to 0} r^2 v \frac{\partial v}{\partial r} = 0. \tag{2.10}$$

Since in spherical coordinates

$$\Delta = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial^2\phi},$$

where the last two terms multiplied by r^2 is the total angular momentum operator Δ_{S^2} on spherical surface, i.e. the Laplace Beltrami operator. We have

$$\begin{aligned}
\|v\|^2_{H^1(\mathscr{C})} &= -\int_{\mathscr{C}} v\Delta v + \int_\Gamma v\left.\frac{\partial v}{\partial r}\right|_{r=R} + \int_{\mathscr{C}} v^2 \\
&= \int_0^R r^2 dr \int_{S^2}\left(v^2 + (\frac{\partial v}{\partial r})^2\right) - \int_0^R dr\int_{S^2}(v\Delta_{S^2}v) \\
&\le 2\pi^2R^2\int_{S^2}\|v\|^2_{H^1([0,R])} + \int_0^R \|v\|^2_{H^1(S^2)}dr \\
&\le C\|v\|_{H^1([0,R]\times S^2)},
\end{aligned}$$

where Green's formula and (2.10) are used for the second equality. This completes the proof. □

3 Error estimates for linear Schrödinger type equations

In this section, we consider a nonconforming approximation for the linear problem (2.2) and apply the analysis to augmented methods under the same framework. Define the nonconforming space

$$H^{\delta}_{\#}(\Omega) = \left\{ v \in L^2_{\#}(\Omega) \ : \ v|_{\mathscr{C}} \in H^1(\mathscr{C}),\ v|_{\mathscr{D}} \in H^1(\mathscr{D}),\ \text{and } b(v_\delta, \psi) = 0,\ \ \forall\ \psi \in M_L \right\} \quad (3.1)$$

equipped with the broken Sobolev norm

$$\|v\|_\delta = \|v\|_{H^1(\mathscr{C})} + \|v\|_{H^1(\mathscr{D})},$$

where $M_L = \text{span}\{Y_{lm},\ 0 \le l \le L, |m| \le l\}$ and the bilinear form $b : \mathcal{S}^K_{NL}(\Omega) \times L^2(S^2)$ is given by

$$b(v, \psi) = \int_\Gamma \psi(v^+ - v^-) d\Gamma$$

with $v^\pm$ the traces of v taken from inside and outside the sphere. The bases set of the following nonconforming method and the augmented methods both belong to the space $H^{\delta}_{\#}(\Omega)$.

3.1 A nonconforming method

Denote by $\mathcal{P}_K(\mathscr{D})$ the space of functions on $\mathscr{D}$ expanded by plane waves

$$\mathcal{P}_K(\mathscr{D}) = \left\{ u \in H^1(\mathscr{D}) : \ u(\mathbf{r}) = \sum_{|\mathbf{k}| \le \frac{2\pi}{L} K} c_{\mathbf{k}} e_{\mathbf{k}}(\mathbf{r})|_{\mathscr{D}} \right\}$$

and $\mathcal{B}_{NL}(\mathscr{C})$ the space of functions on $\mathscr{C}$ expanded by polynomials time spherical harmonics

$$\mathcal{B}_{NL}(\mathscr{C}) = \left\{ u \in H^1(\mathscr{C}) : \ \check{u}(r, \theta, \phi) = \sum_{0 \le n \le N, 0 \le l \le L, |m| < l} c_{nlm} \chi_n(r) Y_{lm}(\theta, \phi) \right\},$$

where $\{\chi_i\}_{i=0}^N$ are bases of polynomial space with degree no greater than N. Since $\chi_i(r) Y_{lm}(\theta, \phi) \notin H^1(\mathscr{C})$ if $l \neq 0$ and $\chi(0) \neq 0$, we take $\chi_0(r) = 1 - \dfrac{r}{R}$ and the rest χ_is vanish at 0, i.e. $\chi_i(0) = 0$ for $1 \le i \le N$. Therefore, we can reformulate the space $\mathcal{B}_{NL}(\mathscr{C})$ as

$$\mathcal{B}_{NL}(\mathscr{C}) = \left\{ u \in H^1(\mathscr{C}) : \ \check{u}(r, \theta, \phi) = c_0 \chi_0(r) + \sum_{1 \le n \le N, 0 \le l \le L, |m| < l} c_{nlm} \chi_n(r) Y_{lm}(\theta, \phi) \right\},$$

where all such combinations belong to $H^1(\mathscr{C})$.

Let us denote

$$\mathcal{S}^K_{NL}(\Omega) = \mathcal{P}_K(\mathscr{D}) \oplus \mathcal{B}_{NL}(\mathscr{C}) = \left\{ u \in L^2_{\#}(\Omega) : \ u|_{\mathscr{C}} \in \mathcal{B}_{NL}(\mathscr{C}) \text{ and } u|_{\mathscr{D}} \in \mathcal{P}_K(\mathscr{D}) \right\} \quad (3.2)$$

and the nonconforming approximation space as

$$V_\delta(\Omega) = H^\delta_\#(\Omega) \cap \mathcal{S}^K_{NL}(\Omega). \tag{3.3}$$

Note that $V_\delta(\Omega) \nsubseteq H^1_\#(\Omega)$. The nonconforming approximation of (2.2) is: Find $\lambda_\delta \in \mathbb{R}$ and $0 \neq u_\delta \in V_\delta$ such that $\|u\|_{L^2(\Omega)=1}$ and

$$a_\delta(u_\delta, v) = \lambda_\delta(u_\delta, v) \quad \forall\ v \in V_\delta, \tag{3.4}$$

where

$$a_\delta(u, v) = \frac{1}{2}\int_{\mathscr{C}} \nabla u \cdot \nabla v + \frac{1}{2}\int_{\mathscr{D}} \nabla u \cdot \nabla v + \int_\Omega V_{eff} uv.$$

We come to construct a bases of the nonconforming space V_δ in the way of augmented methods. Let the bases functions $\{\chi_n\}_{n=0}^N$ on $[0, R]$ span the space of polynomials with degree no greater than N satisfying (see Figure 3.1)

$$\chi_0(r) = 1 - \frac{r}{R}, \quad \chi_i(r)|_{r=R} = 0 \quad \text{for} \quad i = 1, \cdots, N-1, \quad \text{and} \quad \chi_N(r) = \frac{r}{R}. \tag{3.5}$$

We have that the subspace $\tilde{\mathcal{B}}_{NL} \subset \mathcal{B}_{NL}$ defined by

$$\tilde{\mathcal{B}}_{NL} = \left\{ u \in H^1_0(\mathscr{C}) :\ \breve{u}(r, \theta, \phi) = c_0\chi_0(r) + \sum_{1\le n\le N-1, 0\le l\le L, |m|\le l} c_{nlm}\chi_n(r) Y_{lm}(\theta, \phi) \right\}$$

is a finite dimensional discretization of $H^1_0(\mathscr{C})$.

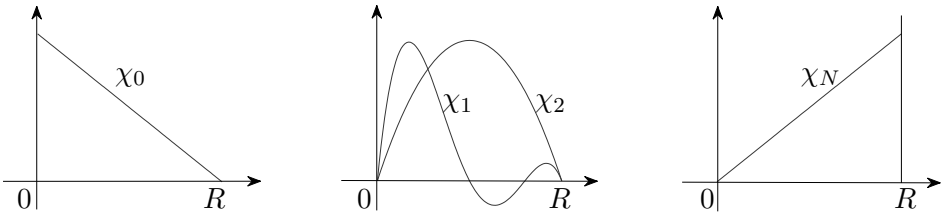

Figure 3.2: Schematic plot of the radial bases $\chi_i(r)$ $i = 0, \cdots, N$ satisfying (3.5).

Define

$$\omega_{\mathbf{k}}(\mathbf{r}) = \begin{cases} |\Omega|^{-\frac{1}{2}} e^{-i\mathbf{k}\cdot\mathbf{r}} & \text{in } \mathscr{D}, \\ \displaystyle\sum_{lm}^{L} \beta^{\mathbf{k}}_{lm}\chi_N(r)\tilde{Y}_{lm}(\mathbf{r}) & \text{in } \mathscr{C}, \end{cases}$$

where the coefficients

$$\beta^{\mathbf{k}}_{lm} = 4\pi i^l j_l(kR)\tilde{Y}^*_{lm}(\mathbf{k})/\chi_N(R) \tag{3.6}$$

are determined by the continuity constraint in (3.1) together with the scattering expansion [37]

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{lm} i^l j_l(kr)\tilde{Y}^*_{lm}(\mathbf{k})\tilde{Y}_{lm}(\mathbf{r}). \tag{3.7}$$

Set $\tilde{V}_\delta = \tilde{\mathcal{B}}_{NL} \oplus \text{span}\{\omega_{\mathbf{k}}(\mathbf{r}) : \ |\mathbf{k}| \le K\}$. It is obvious from the definition of $\omega_{\mathbf{k}}$ that $\tilde{V}_\delta \subset V_\delta$, which together with the fact

$$\dim(V_\delta) = \dim(\mathcal{P}_K) + \dim(\mathcal{B}_{NL}) - \dim(M_L) = \dim(\mathcal{P}_K) + \dim(\tilde{\mathcal{B}}_{NL}) = \dim(\tilde{V}_\delta)$$

implies $V_\delta = \tilde{V}_\delta$. Having a set of bases that span V_δ, we can derive the error of a best approximation in this finite dimensional space.

Denote for simplicity by $\varrho = \min\{K, N, L\}$, we have

Lemma 3.1. *If $u \in H^s(\mathscr{D}) \oplus H^s([0,R]\times S^2)$ for $s \in \mathbb{R}_+$, then there exists a constant C such that*

$$\inf_{v_\delta \in V_\delta} \|u - v_\delta\|_\delta \le C\varrho^{-(s-3/2)}(\|u\|_{H^s(\mathscr{D})} + \|u\|_{H^s([0,R]\times S^2)}). \tag{3.8}$$

Proof. Split u into three parts $u = u_1 + u_2 + u_3$ such that

$$u_1(\mathbf{r}) = \begin{cases} u(0)\cdot(1-r/R) & \text{in } \mathscr{C} \\ 0 & \text{in } \mathscr{D} \end{cases}, \qquad u_2(\mathbf{r}) = \begin{cases} \check{u}(R,\theta,\phi)\cdot r/R & \text{in } \mathscr{C} \\ u & \text{in } \mathscr{D} \end{cases}$$

and $u_3 = u - u_1 - u_2$ where $\check{u}(R,\theta,\phi)$ is defined in the sense of trace. We approximate these three parts separately.

First, u_1 is approximated exactly by

$$u_1(\mathbf{r}) = v_{1\delta}(\mathbf{r}) \equiv u(0)\chi_0(r). \tag{3.9}$$

To approximate u_2, we shall first extend $u_2|_{\mathscr{D}}$ smoothly into the sphere $\mathscr{C}$. Since u can be represented by

$$u(\mathbf{r}) = \sum_{lm}^{\infty} u_{lm}(r)\tilde{Y}_{lm}(\mathbf{r})$$

around the sphere surface with $u_{lm}(r) = \displaystyle\int_0^\pi \int_0^{2\pi} u(r,\theta,\phi)Y_{lm}(\theta,\phi)\sin(\theta)d\theta d\phi$, we can define

$$\tilde{u}(\mathbf{r}) = \begin{cases} u(\mathbf{r}) & \text{in } \mathscr{D}, \\ \displaystyle\sum_{lm}^{\infty} \varphi_{lm}(r)Y_{lm}(\theta,\phi) & \text{in } \mathscr{C}, \end{cases} \tag{3.10}$$

where $\varphi_{lm}(r) = \tau(r)\displaystyle\sum_{n=1}^{s+1} c_n u_{lm}(R + \frac{1}{n}(R-r))$ with the coefficients c_n satisfying $\displaystyle\sum_{n=1}^{s+1}(-\frac{1}{n})^k c_n = 1$ $(k = 0, 1, \cdots, s)$, and $\tau \in C^\infty([0,R])$ satisfying $\tau = 0$ in $[0, \frac{R}{3}]$ and $\tau = 1$ in $[\frac{2R}{3}, R]$. We observe that $u \in H^s(\mathscr{D})$ leads to $\tilde{u} \in H^s(\Omega)$ and moreover

$$\|\tilde{u}\|_{H^s(\Omega)} \le \beta_s \|u\|_{H^s(\mathscr{D})}, \tag{3.11}$$

where the constant β_s is only related to s, R and $\|\tau\|_{H^s[0,R]}$. Let

$$\tilde{u}_K = \sum_{|\mathbf{k}|\le K} \tilde{c}_{\mathbf{k}} e_{\mathbf{k}} \quad \text{and} \quad v_{2\delta} = \sum_{|\mathbf{k}|\le K} \tilde{c}_{\mathbf{k}} \omega_{\mathbf{k}} \quad \text{with} \quad \tilde{c}_{\mathbf{k}} = \int_\Omega e_{\mathbf{k}}(\mathbf{r})\tilde{u}(\mathbf{r})d\mathbf{r}, \tag{3.12}$$

we have from (3.11) that

$$\begin{aligned} \|u_2 - v_{2\delta}\|_{H^1(\mathscr{D})} &= \|\tilde{u} - \tilde{u}_K\|_{H^1(\mathscr{D})} \le \|\tilde{u} - \tilde{u}_K\|_{H^1(\Omega)} \\ &\le CK^{-(s-1)}\|\tilde{u}\|_{H^s(\Omega)} \le C\beta_s K^{-(s-1)}\|u\|_{H^s(\mathscr{D})}. \end{aligned} \tag{3.13}$$

Using Lemma 2.3, the definition of $\omega_{\mathbf{k}}$, and the trace theorem, we have

$$\begin{aligned} \|u_2 - v_{2\delta}\|_{H^1(\mathscr{C})} &\lesssim \|u_2 - v_{2\delta}\|_{H^1([0,R]\times S^2)} \\ &= \|\chi_N(r)\big(\check{u}_2(R,\theta,\phi) - \check{v}_{2\delta}(R,\theta,\phi)|_{\mathscr{C}}\big)\|_{H^1([0,R]\times S^2)} \\ &\le C\|u_2 - v_{2\delta}|_{\mathscr{C}}\|_{H^1(\Gamma)} \\ &\le C(\|v_{2\delta}|_{\mathscr{C}} - v_{2\delta}|_{\mathscr{D}}\|_{H^1(\Gamma)} + \|u_2 - v_{2\delta}|_{\mathscr{D}}\|_{H^1(\Gamma)}) \\ &\le C(L^{-(s-3/2)}\|v_{2\delta}\|_{H^s(\mathscr{D})} + \|u_2 - v_{2\delta}\|_{H^{3/2}(\mathscr{D})}), \end{aligned}$$

which together with (3.13) leads to

$$\|u_2 - v_{2\delta}\|_\delta \le C(L^{-(s-3/2)} + K^{-(s-3/2)})\|u_2\|_{H^s(\Omega)}. \tag{3.14}$$

For the third part, Define the projection $P_N : H_0^1([0,R]) \to \Psi_N = \text{span}\{\chi_i, 1 \le i \le N-1\}$ satisfying

$$(\nabla(v - P_N v), \nabla\psi) = 0 \quad \forall\ \psi \in H_0^1([0,R])$$

and the projection $P_L : L^2(S^2) \to \mathcal{Y}_L = \text{span}\{Y_{lm}, 0 \le l \le L, -l \le m \le m\}$ by

$$P_L\varphi(\theta,\phi) = \sum_{l=0}^{L} \hat{\varphi}_{lm} Y_{lm}(\theta,\phi) \quad \text{with} \quad \hat{\varphi}_{lm} = \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi\ \varphi(\theta,\phi)Y_{lm}(\theta,\phi).$$

Define the projection $\mathbb{P}^{NL} : H^1([0,R]\times S^2) \to \Psi_N \times \mathcal{Y}_L$ by $\mathbb{P}^{NL} = P_N \circ P_L$. Since the polynomials and spherical harmonic approximations have the following convergence rates

$$\|v - P_N v\|_{H^1([0,R])} \le CN^{-(s-1)}\|v\|_{H^s([0,R])},$$

$$\|\varphi - P_L\varphi\|_{H^1(S^2)} \le CL^{-(s-1)}\|\varphi\|_{H^s(S^2)},$$

we obtain that for $u_3 \in H^s([0,R]\times S^2)$,

$$\|u_3 - \mathbb{P}^{NL}u_3\|_{H^1([0,R]\times S^2)} \le C(L^{-(s-1)} + N^{-(s-1)})\|u_3\|_{H^s([0,R]\times S^2)}. \tag{3.15}$$

Taking $v_{3\delta} = \mathbb{P}^{NL}u_3$, we have from Lemma 2.3 and (3.15) that

$$\begin{aligned} \|u_3 - v_{3\delta}\|_{H^1(\mathscr{C})} &\le \|u_3 - v_{3\delta}\|_{H^1([0,R]\times S^2)} \\ &\le C(L^{-(s-1)} + N^{-(s-1)})\|u_3\|_{H^s([0,R]\times S^2)}. \end{aligned} \tag{3.16}$$

Taking (3.9), (3.14), (3.16) and the fact $v_{1\delta} + v_{2\delta} + v_{3\delta} \in V_\delta$ into accounts, we derive (3.8) directly, which completes the proof. □

Remark 3.1. *We shall mention that the error estimate we obtain in Lemma 3.1 may not be optimal, which is half order lower than the optimal expectation, i.e. one would expect $s-1$ instead. Nevertheless, if the function u has sufficiently high regularity, say, s could be arbitrarily large, then we may be satisfied with this convergence rate.*

Define the operator $T : L^2_{\#}(\Omega) \to H^1_{\#}(\Omega)$ such that $\forall\ f \in X$,

$$a(Tf, v) = (f, v) \quad \forall\ v \in H^1_{\#}(\Omega). \tag{3.17}$$

Then (2.2) is equivalent to the operator form $Tu = \lambda^{-1}u$. We also define the operator $T_\delta : L^2_{\#}(\Omega) \to V_\delta$ such that $\forall\ f \in L^2_{\#}(\Omega)$,

$$a_\delta(T_\delta f, v) = (f, v) \quad \forall\ v \in V_\delta, \tag{3.18}$$

and (3.4) is equivalent to $T_\delta u_\delta = \lambda_\delta^{-1} u_\delta$. One can prove that T and T_δ are self-adjoint operators and satisfy the following lemma.

Lemma 3.2. *If $Tf \in H^s(\mathscr{D}) \oplus H^s([0,R] \times S^2)$ for $f \in L^2_{\#}(\Omega)$, then*

$$\|Tf - T_\delta f\|_\delta \le C\varrho^{-(s-3/2)}(\|Tf\|_{H^s(\mathscr{D})} + \|Tf\|_{H^s([0,R]\times S^2)}). \tag{3.19}$$

Proof. Denote $u = Tf$ and $u_\delta = T_\delta f$. Processing in a standard way (see, e.g. [10, 11, 39]), we get

$$\|u - u_\delta\|_\delta \le C\left(\inf_{v_\delta \in V_\delta} \|u - v_\delta\|_\delta + \sup_{v_\delta \in V_\delta} \frac{a_\delta(u - u_\delta, v_\delta)}{\|v\|_\delta}\right) \tag{3.20}$$

and

$$a_\delta(u - u_\delta, v_\delta) = b(v_\delta, \varphi - \psi_L) \quad \forall\ v_\delta \in \mathcal{S}^K_{NL}, \quad \forall\ \psi_L \in M_L$$

with $\varphi = \dfrac{\partial u}{\partial n}$, which together imply

$$\|u - u_\delta\|_\delta \le C\left(\inf_{v_\delta \in V_\delta} \|u - v_\delta\|_\delta + \sup_{v_\delta \in V_\delta} \inf_{\psi_L \in M_L} \frac{b(v_\delta, \varphi - \psi_L)}{\|v\|_\delta}\right). \tag{3.21}$$

The first term of the right hand side involved in (3.21) is the best approximation error which has been given in Lemma 3.1, the second term is nothing else than the consistency error, which indicate the variational crime committed by the nonconforming discretization.

For the consistency error, we have that $\forall\ \psi_L \in M_L$,

$$\begin{aligned} b(v_\delta, \varphi - \psi_L) &= \int_\Gamma (v_\delta^+ - v_\delta^-)(\varphi - \psi_L) \\ &\le \inf_{\psi_L \in M_L} \|\varphi - \psi_L\|_{H^{-\frac{1}{2}}(\Gamma)} \|v_\delta^+ - v_\delta^-\|_{H^{\frac{1}{2}}(\Gamma)} \\ &\le CL^{-(s-1)} \|\frac{\partial u}{\partial n}\|_{H^{s-3/2}(\Gamma)} (\|v_\delta\|_{H^1(\mathscr{C})} + \|v_\delta\|_{H^1(\mathscr{D})}) \\ &\le CL^{-(s-1)} \|u\|_{H^s(\mathscr{D})} \|v_\delta\|_\delta, \end{aligned} \tag{3.22}$$

where the trace inequality is used.

Taking (3.8), (3.21) and (3.22) into accounts, we obtain (3.19), which completes the proof. □

Denote by $\vartheta(T)$ the spectrum and $\rho(T)$ the resolvent set respectively of the solution operator T. For any $z \in \mathbb{C}$ in $\rho(T)$, we define the resolvent operator $R_z(T) = (z - T)^{-1}$. Let λ be an eigenvalue of T and γ be a circle in the complex plane centered at λ^{-1} which does not enclose any other point of $\vartheta(T)$. We define the operators $\mathscr{E}$ and $\mathscr{E}_\delta$ by

$$\mathscr{E} = \mathscr{E}(\lambda) = \frac{1}{2\pi i}\int_\gamma R_z(T)dz, \quad \mathscr{E}_\delta = \mathscr{E}_\delta(\lambda) = \frac{1}{2\pi i}\int_\gamma R_z(T_\delta)dz.$$

If K, N, L are sufficiently large, then $\mathscr{E}$ and $\mathscr{E}_\delta$ are the spectral projector of T and T_δ respectively relative to λ^{-1}.

To evaluate the distance between eigenspaces, we need a suitable notation. For X and Y closed subspaces of $H^\delta_{\#}(\Omega)$, we denote (see, e.g. [38])

$$\hat{\delta}(X, Y) := \sup_{x\in X,\ \|x\|_{L^2(\Omega)}=1} \inf_{y\in Y,\ \|y\|_{L^2(\Omega)}=1} \|x - y\|_\delta$$

and denote the gap between X and Y as

$$\mathfrak{G}(X, Y) = \max\{\hat{\delta}(X, Y), \hat{\delta}(Y, X)\}.$$

The following theorem is the main result of this section, which states the convergence rates of the nonconforming eigenvalue approximations.

Theorem 3.1. *Let λ be an eigenvalue of (2.2) with $\dim(R(\mathcal{E})) = m$, where R denotes the range. If ϱ is sufficiently large, then there exist m eigenvalues $\lambda_{1,\delta}, \cdots, \lambda_{m,\delta}$ such that*

$$\sup_{1\le j\le m} |\lambda - \lambda_{j,\delta}| + \mathfrak{G}(R(\mathcal{E}), R(\mathcal{E}_\delta)) \le C\varrho^{-(s-3/2)}. \tag{3.23}$$

Proof. Note that for $f \in L^2_{\#}(\Omega)$, $Tf \in H^2(\Omega)$ and $\|Tf\|_{H^2(\Omega)} \le C\|f\|_{L^2(\Omega)}$. By Sobolev' imbedding theorem $H^2(\Omega) \hookrightarrow C^{\frac{1}{2}-\varepsilon}(\Omega)$ for any $\varepsilon > 0$, we have $Tf \in H^\sigma([0, R] \times S^2)$ for $0 < \sigma < \frac{1}{2}$ and $\|Tf\|_{H^\sigma([0,R]\times S^2)} \le C\|Tf\|_{H^2(\mathscr{C})}$.

Using similar arguments as that in the proof of Lemma 3.1, we can derive the following L^2 error estimate

$$\begin{aligned}\inf_{v_\delta\in V_\delta} \|v - v_\delta\|_{L^2(\Omega)} &\le C\big((K^{-(3/2)} + L^{-(3/2)})\|v\|_{H^2(\mathscr{D})} + (N^{-\sigma} + L^{-\sigma})\|v\|_{H^\sigma([0,R]\times S^2)}\big)\\ &\le C\varrho^{-\sigma}\|v\|_{H^2(\Omega)} \quad \forall v \in H^2(\Omega),\end{aligned}$$

which together with the Aubin-Nitsche technique leads to

$$\begin{aligned}\|T - T^\delta\|_{\mathscr{L}(L^2_{\#}(\Omega),L^2_{\#}(\Omega))} &= \sup_{f\in L^2_{\#}(\Omega),\|f\|_{L^2(\Omega)}=1} \sup_{g\in L^2_{\#}(\Omega),\|g\|_{L^2(\Omega)}=1} |((T - T^\delta)f, g)|\\ \le \sup_{f\in L^2_{\#}(\Omega),\|f\|_{L^2(\Omega)}=1} &\|Tf - T^\delta f\|_{H^2(\Omega)} \sup_{g\in L^2_{\#}(\Omega),\|g\|_{L^2(\Omega)}=1} \inf_{v_\delta\in V_\delta} \|Tg - v_\delta\|_{L^2(\Omega)}\\ \le C\varrho^{-\sigma} \sup_{f\in L^2_{\#}(\Omega),\|f\|_{L^2(\Omega)}=1} &\|Tf - T^\delta f\|_{H^2(\Omega)} \sup_{g\in L^2_{\#}(\Omega),\|g\|_{L^2(\Omega)}=1} \|Tg\|_{H^2(\Omega)}.\end{aligned}$$

Hence we have

$$\lim_{\varrho\to\infty}\|T-T^{\delta}\|_{\mathscr{L}(L^2_{\#}(\Omega),L^2_{\#}(\Omega))}\leq C\lim_{\varrho\to\infty}\varrho^{-\sigma}=0. \tag{3.24}$$

Using (3.24) and the result in [38, Theorem 1], we have the convergence of the eigenvalues and

$$\mathfrak{G}(R(\mathcal{E}),R(\mathcal{E}_\delta))\lesssim\|T-T^{\delta}\|_{\mathscr{L}(R(\mathcal{E}),V_\delta)},$$

and it is only necessary for us to estimate the righthand side term. Since

$$\begin{aligned}\|\mathscr{E}-\mathscr{E}_\delta\|_{\mathscr{L}(R(\mathscr{E}),V_\delta)} &\leq \sup_{v\in R(\mathscr{E}),\|v\|_{L^2(\Omega)}=1}\|Tv-T^{\delta}v\|_{\delta}\\ &\leq C\varrho^{-(s-3/2)}\sup_{v\in R(\mathscr{E}),\|v\|_{L^2(\Omega)}=1}(\|v\|_{H^s(\mathscr{D})}+\|v\|_{H^s([0,R]\times S^2)})\\ &\leq C\varrho^{-(s-3/2)}\qquad\forall\ s\in\mathbb{R}_+,\end{aligned} \tag{3.25}$$

where Lemma 3.2, the regularity result Lemma 2.1, 2.2, and the fact $Tv=\lambda^{-1}v$ for $v\in R(\mathcal{E})$ are used. This completes the proof of error estimates for eigenspace.

For eigenvalue estimates, we obtain the following identity by a simple calculation that

$$\lambda-\lambda_\delta=a_\delta(u-u_\delta,u-u_\delta)-\lambda_\delta(u-u_\delta,u-u_\delta)+2D_\delta \tag{3.26}$$

with the consistency error

$$D_\delta=a_\delta(u_\delta,u)-\lambda_\delta(u_\delta,u)=a_\delta(u_\delta,u-v_\delta)-\lambda_\delta(u_\delta,u-v_\delta)\quad\forall\ v_\delta\in V_\delta. \tag{3.27}$$

Using again Lemma 2.1, 2.2 and 3.2, we have

$$|D_\delta|\leq C\inf_{v_\delta\in V_\delta}\|u-v_\delta\|_\delta\leq C\varrho^{-(s-3/2)}\quad\forall\ s\in\mathbb{R}_+.$$

For any eigenpair $(\lambda_\delta,u_{j,\delta})$ of (3.4), we can find an eigenfunction $u\in R(\mathscr{E})$ and $\|u\|_{L^2(\Omega)}=1$, such that $\|u_{j,\delta}-u\|_\delta\leq C\varrho^{-(s-3/2)}$. This together with (3.26) and (3.27) leads to $|\lambda-\lambda_{j,\delta}|\leq C\varrho^{-(s-3/2)}$, which completes the proof. □

3.2 APW methods

The APW method can be viewed as a modified method of the nonconforming scheme under the assumption that the effective potential is spherical symmetric inside the atomic sphere $\mathscr{C}$, say $V_{eff}(\mathbf{r})=V(r)$ for $r\leq R$. It takes $\tilde{\mathcal{B}}_{NL}=\emptyset$ and use $\chi_l(r,\lambda_\delta)$ instead of χ_0, where $\chi_l(r,\lambda_\delta)$ is the regular solution of

$$-\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\chi_l}{dr}\right)+\left(\frac{l(l+1)}{r^2}+V(r)-\lambda_\delta\right)\chi_l=0 \tag{3.28}$$

with λ_δ the eigenvalue of the underlying discrete problem. The approximation space is $V_\delta = \tilde{V}_{KL} = \text{span}\{\omega_{\mathbf{k}}^{\lambda_\delta}\}_{|\mathbf{k}|\le K}$ with

$$\omega_{\mathbf{k}}^{\lambda_\delta}(\mathbf{r}) = \begin{cases} |\Omega|^{-\frac{1}{2}} e^{-i\mathbf{k}\cdot\mathbf{r}} & \text{in } \mathscr{D}, \\ \displaystyle\sum_{lm}^{L} \alpha_{lm}^{\mathbf{k}} \chi_l(r, \lambda_\delta) \tilde{Y}_{lm}(\mathbf{r}) & \text{in } \mathscr{C}, \end{cases} \tag{3.29}$$

where the coefficients $\alpha_{lm}^{\mathbf{k}}$ are determined by the expansion (3.7) as

$$\alpha_{lm}^{\mathbf{k}} = 4\pi i^l j_l(kR) \tilde{Y}_{lm}^*(\mathbf{k}) / \chi_l(R, \lambda_\delta) \tag{3.30}$$

so that the constraint in (3.1) is satisfied.

The task of finding the APW eigenvalues becomes somewhat troublesome due to the asymptote problem (see [40]): The energy dependent APW bases functions must be evaluated for a large number of energy parameters, and sometimes one might hit an energy parameter for which $\chi_l(r, \lambda)$ equals zero at the spherical surface. Inserted in the evaluation of the APW matching coefficients (3.30) will yield infinite $\alpha_{lm}^{\mathbf{k}}$, which decouples the bases set at the spherical surface. Therefore, we shall always assume that λ is not the eigenvalue for which $\chi_l(R, \lambda) = 0$, which can be achieved by varying the radii of atomic spheres.

Since the bases functions depend on the eigenvalue λ_δ which is of course not known before diagonalization, a different energy dependent sets of APW bases must be found for each eigenvalue. This leads to a nonlinear eigenvalue problem

$$H(\lambda_\delta) u_\delta = \lambda_\delta u_\delta, \tag{3.31}$$

which is computationally very demanding. Using the root-tracing method [36], one has to choose an energy parameter, solve the radial Schrödinger equation to obtain the APW bases and set up the matrix elements. The determinant has to be computed, which should vanish according to the secular equation (3.31) but did not with a incorrect eigenvalue parameter. One has to vary the trial energy parameter to numerically find the zeros of this determinant (see e.g. Example 2 in Section 5). This is the main drawback of APW scheme which at best work for simple systems with few eigenvalues only.

In the following, we shall give a convergence analysis of the APW approximations. By the APW methods, we search the eigenvalue approximations in a finite domain that contain the bands of interest for each given K, L. Therefore, we have limiting point in this domain when K and L go to infinity. Let λ_∞ be a accumulation point, i.e., there exists a sequence of eigenpairs $\{(\lambda_{\delta,k}, u_{\delta,k})\}_{k\in\mathbb{Z}_+}$ such that

$$\lim_{k\to\infty} |\lambda_{\delta,k} - \lambda_\infty| = 0. \tag{3.32}$$

Since the assumption (2.8) implies

$$\begin{aligned}\lambda_\delta &= a_\delta(u_\delta,u_\delta)\\ &\geq \|u_\delta\|^2_{H^1(\mathscr{C})}+\|u_\delta\|^2_{H^1(\mathscr{D})}-\|\frac{Z}{|\mathbf{r}|}\|_{L^2(\Omega)}\|u_\delta\|^{1/2}_{L^2(\Omega)}\|u_\delta\|^{3/2}_{L^6(\Omega)}\\ &\quad -\|\rho\|_{L^2(\Omega)}\|\frac{1}{|\mathbf{r}|}\|_{L^2(\Omega)}\|u_\delta\|^2_{L^2(\Omega)}-\|v_s\|_{L^\infty(\Omega)}\|u_\delta\|^2_{L^2(\Omega)}\\ &\geq c\|u_\delta\|_\delta - C\|u_\delta\|_{L^2(\Omega)}\end{aligned}$$

for some constant c and C, we have that $\{u_{\delta,k}\}$ is a bounded sequence in $H^\delta_\#$. Banach-Alaoglu Theorem yields that there exists a weakly convergent subsequence, which we still denote by $\{u_{\delta,k}\}_{k\in\mathbb{Z}_+}$, such that

$$u_{\delta,k}\rightharpoonup u_\infty \quad \text{for some} \quad u_\infty\in H^1_\#(\Omega). \tag{3.33}$$

Using Sobolev's imbedding theorem, we have that $u_{\delta,k}$ converge to u_∞ in $L^q(\Omega)$ for $1\leq q<6$. This can lead to

$$\lim_{k\to\infty}\int_\Omega V_{eff}(\mathbf{r})(u^2_\infty-u^2_{\delta,k})d\mathbf{r}=0.$$

Therefore, we derive from (3.32) that $\|u_{\delta,k}\|_\delta\to\|u_\infty\|_\delta$, which together with (3.33) yields

$$u_{\delta,k}\to u_\infty \quad \text{in} \quad H^\delta_\#(\Omega).$$

Theorem 3.2. *If $V_{eff}(\mathbf{r})$ is a spherical symmetric potential in $\mathscr{C}$, then the limiting pair $(\lambda_\infty,u_\infty)$ is an eigenpair of (2.2), that is*

$$a(u_\infty,v)=\lambda_\infty(u_\infty,v)\quad\forall\ v\in H^1_\#(\Omega). \tag{3.34}$$

Moreover, for the sequence of eigenparis $\{(\lambda_\delta,u_\delta)\}$ that converge to $(\lambda_\infty,u_\infty)$, there holds

$$|\lambda_\infty-\lambda_\delta|+\|u_\infty-u_\delta\|_\delta\leq C(K^{-(s-3/2)}+L^{-(s-3/2)})\quad\forall\ s\in\mathbb{R}_+ \tag{3.35}$$

for sufficiently large K and L.

Proof. Since $V_{eff}(\mathbf{r})=V(r)$ and $\chi_l(r,\lambda_\delta)$ satisfies the radial Schrödinger equation, we have that for $\breve{\varphi}(r,\theta,\phi)=\sum_{lm}c_{lm}u_\varepsilon(r)Y_{lm}(\theta,\phi)$

$$(-\frac{1}{2}\Delta+V_{eff})\varphi=\lambda_\delta\varphi.$$

Denote by $a_{\mathscr{C}}(w,v)=\frac{1}{2}\int_{\mathscr{C}}\nabla w\cdot\nabla v+\int_{\mathscr{C}}V_{eff}wv$ and $a_{\mathscr{D}}(w,v)=\frac{1}{2}\int_{\mathscr{D}}\nabla w\cdot\nabla v+\int_{\mathscr{D}}V_{eff}wv$. For any $v\in C^\infty_\#(\Omega)$, we have

$$\begin{aligned}a_\delta(u_\delta,v)-\lambda_\delta(u_\delta,v) &= a_\delta(u_\delta,v_\delta)-\lambda_\delta(u_\delta,v_\delta)+a_\delta(u_\delta,v-v_\delta)-\lambda_\delta(u_\delta,v-v_\delta)\\ &= a_{\mathscr{C}}(u_\delta,v-v_\delta)+a_{\mathscr{D}}(u_\delta,v-v_\delta)-\lambda_\delta(u_\delta,v-v_\delta)\\ &= \int_\Gamma\frac{\partial u|_{\mathscr{C}}}{\partial n}(v-v_\delta|_{\mathscr{C}})+a_{\mathscr{D}}(u_\delta,v-v_\delta)-\lambda_\delta(u_\delta,v-v_\delta)_{\mathscr{D}}\\ &\lesssim (\|v-v_\delta|_{\mathscr{D}}\|_{H^1(\mathscr{D})}+\|v_\delta|_{\mathscr{C}}-v_\delta|_{\mathscr{D}}\|_{H^{1/2}(\Gamma)})\|u\|_\delta \qquad\forall\ v_\delta\in\tilde{V}_{KL}.\end{aligned}$$

Using standard Fourier expansion coefficients, we can find $v_\delta \in \tilde{V}_{KL}$ such that $\|v-v_\delta\|_{H^1(\mathscr{D})} \to 0$ when $K \to \infty$, which together with the fact $\lim_{L\to\infty} \|v_\delta|_{\mathscr{C}} - v_\delta|_{\mathscr{D}}\|_{H^{1/2}(\Gamma)} = 0$ leads to

$$\lim_{K,L\to\infty} a_\delta(u_\delta, v) - \lambda_\delta(u_\delta, v) = 0 \quad \forall\ v \in C^\infty_\#(\Omega). \tag{3.36}$$

Since $C^\infty_\#(\Omega)$ is dense in $H^1_\#(\Omega)$, we have that (3.36) holds for all $v \in H^1_\#(\Omega)$.

Note that

$$\begin{aligned} & |a(u_\infty, v) - \lambda_\infty(u_\infty, v)| \ = \ |a_\delta(u_\infty, v) - \lambda_\infty(u_\infty, v)| \\ \le \ & |a_\delta(u_\infty - u_\delta, v)| + |\lambda_\infty(u_\infty - u_\delta, v)| + |(\lambda_\delta - \lambda_\infty)(u_\delta, v)| + |a_\delta(u_\delta, v) - \lambda_\delta(u_\delta, v)| \\ \le \ & \|u_\infty - u_\delta\|_\delta + |\lambda_\infty - \lambda_\delta| + |a_\delta(u_\delta, v) - \lambda_\delta(u_\delta, v)| \qquad \forall\ v \in H^1_\#(\Omega). \end{aligned}$$

Using (3.36) and the convergence of u_δ to u_∞ in $H^\delta_\#(\Omega)$ and λ_δ to λ_∞, we can conclude (3.34).

To estimate the convergence rate of eigenfunctions, it is only necessary for us to estimate $\|T - T_\delta\|_{\mathscr{L}(R(\mathcal{E}),V_\delta)}$.

Denote by $A_l = -\frac{1}{r^2}\frac{d}{dr}(r^2\frac{d\chi_l}{dr}) + \frac{l(l+1)}{r^2} + V(r)$, $\chi_l^\lambda = \chi_l(r,\lambda)$ and $\chi_l^{\lambda_\delta} = \chi_l(r,\lambda_\delta)$ for simplicity. If $(\lambda_\delta, \chi_l^{\lambda_\delta})$ satisfies $(A_l - \lambda_\delta)\chi_l^{\lambda_\delta} = 0$ and $(\lambda, \chi_l^\lambda)$ satisfies $(A_l - \lambda)\chi_l^\lambda = 0$ with the same Dirichlet boundary condition, then we have

$$\begin{cases} (A_l - \lambda)(\chi_l^\lambda - \chi_l^{\lambda_\delta}) = (\lambda - \lambda_\delta)\chi_l^{\lambda_\delta} \quad \text{in} \ \ [0,R], \\ \chi_l^\lambda - \chi_l^{\lambda_\delta}|_{\partial[0,R]} = 0. \end{cases}$$

Since λ is not the eigenvalue of A_l with Dirichlet boundary condition (assumption on the asymptote problem), we can derive

$$\|\chi_l^\lambda - \chi_l^{\lambda_\delta}\|_{H^1([0,R])} \lesssim |\lambda - \lambda_\delta|. \tag{3.37}$$

Let $\tilde{u}(\mathbf{r})$ be the extension of u given as in (3.10) and $\tilde{c}_\mathbf{k} = \int_\Omega e_\mathbf{k}(\mathbf{r})\tilde{u}(\mathbf{r})d\mathbf{r}$, we can define the interpolation

$$I_K^\lambda u = \sum_{|\mathbf{k}|\le K} \tilde{c}_\mathbf{k}\omega_k^\lambda \qquad \text{and} \qquad I_K^{\lambda_\delta} u = \sum_{|\mathbf{k}|\le K} \tilde{c}_\mathbf{k}\omega_k^{\lambda_\delta}.$$

Since $Tu = \lambda^{-1}u$ for $u \in R(\mathcal{E})$, we obtain from (3.20) that

$$\|Tu - T_\delta u\|_\delta \lesssim \|u - I_K^{\lambda_\delta} u\|_\delta + \mathcal{N}_\delta, \tag{3.38}$$

where the interpolation error is estimated by using Lemma 2.3 and (3.37) as

$$\begin{aligned}
\|I_K^{\lambda_\delta}u-u\|_\delta &= \|I_K^{\lambda_\delta}u-u\|_{H^1(\mathscr{D})}+\|I_K^{\lambda}u-u\|_{H^1([0,R]\times S^2)}+\|I_K^{\lambda}u-I_K^{\lambda_\delta}u\|_{H^1([0,R]\times S^2)}\\
&\le \|I_K^{\lambda_\delta}u-u\|_{H^1(\mathscr{D})}+\|\sum_{lm}\chi_l^{\lambda}(r)Y_{lm}(\theta,\phi)\big(\frac{\check{u}(R,\theta,\phi)-I_K^{\lambda_\delta}\check{u}(R,\theta,\phi)}{\chi_l^{\lambda}(R)},\\
&\quad Y_{lm}(\theta,\phi)\big)\|_{H^1([0,R]\times S^2)}+\|\sum_{lm}^{L}\alpha_{lm}^{\mathbf{k}}(\chi_l^{\lambda}(r)-\chi_l^{\lambda_\delta}(r))Y_{lm}(\theta,\phi)\|_{H^1([0,R]\times S^2)}\\
&\lesssim \|I_K^{\lambda_\delta}u-u\|_{H^1(\mathscr{D})}+\|u-I_K^{\lambda}u|_{\mathscr{C}}\|_{H^1(\Gamma)}+\sum_{l=0}^{L}\|\chi_l^{\lambda}-\chi_l^{\lambda_\delta}\|_{H^1([0,R])}\\
&\le \|I_K^{\lambda_\delta}u-u\|_{H^1(\mathscr{D})}+\|I_K^{\lambda}u|_{\mathscr{C}}-I_K^{\lambda}u|_{\mathscr{D}}\|_{H^1(\Gamma)}+\|u-I_K^{\lambda}u\|\|_{H^{3/2}(\mathscr{D})}+|\lambda-\lambda_\delta|\\
&\lesssim L^{-(s-3/2)}+K^{-(s-3/2)}+|\lambda-\lambda_\delta| \qquad (3.39)
\end{aligned}$$

and the consistent error can be obtained as in the proof Lemma 3.2

$$\mathcal{N}_\delta=\sup_{v_\delta\in V_\delta}\frac{a(u-u_\delta,v_\delta)}{\|v\|_\delta}\lesssim L^{-(s-1)}\|u\|_{H^s(\mathscr{D})}. \qquad (3.40)$$

Taking (3.38), (3.39) and (3.40) into account gives rise to

$$\|T-T_\delta\|_{\mathscr{L}(R(\mathcal{E}),V_\delta)}\le C(K^{-(s-3/2)}+L^{-(s-3/2)})+|\lambda-\lambda_\delta|. \qquad (3.41)$$

Using (3.26), we have $|\lambda-\lambda_\delta|\lesssim\|T-T_\delta\|^2_{\mathscr{L}(R(\mathcal{E}),V_\delta)}+D_\delta$, which together with (3.41) and the convergence of eigenpairs leads to our desire result (3.35). This completes the proof. □

Remark 3.2. *When the radius R is well chosen, the assumption of spherical symmetric potential is reasonable for a lot of systems, e.g. close-packed crystal [36]. That is why APW methods has been successfully used in many computations.*

3.3 LAPW and APW+lo methods

Under the nonconforming framework, the LAPW methods take $\tilde{\mathcal{B}}_{NL}=\emptyset$ and use the combination of radial functions $\chi_l(r,E_l)$ and its energy derivative $\dot{\chi}_l(r,E_l)$ with a fixed parameter E_l instead of χ_0, where the energy derivative is defined by

$$\dot{\chi}_l(r,E_l)=\frac{\partial}{\partial E_l}\chi_l(r,\varepsilon)|_{\varepsilon=E_l}$$

with χ_l kept normalized to the same value in the sphere (the properties of $\dot{\chi}_l(r,E_l)$ can be referred to [4, 36, 40]). The approximation space is $V_\delta=\hat{V}_{KL}\equiv\mathrm{span}\{\omega_{\mathbf{k}}\}_{|\mathbf{k}|\le K}$ with

$$\omega_{\mathbf{k}}(\mathbf{r})=\begin{cases}|\Omega|^{-\frac{1}{2}}e^{-i\mathbf{k}\cdot\mathbf{r}} & \text{in } \mathscr{D},\\ \sum_{lm}^{L}[\alpha_{lm}^{\mathbf{k}}\chi_l(r,E_l)+\beta_{lm}^{\mathbf{k}}\dot{\chi}_l(r,E_l)]Y_{lm}(\mathbf{r}) & \text{in } \mathscr{C}.\end{cases} \qquad (3.42)$$

The coefficients $\alpha_{lm}^{\mathbf{k}}$ and $\beta_{lm}^{\mathbf{k}}$ are determined by (3.7) requiring that the bases function matches both the value and slope in the weak sense. The LAPW methods provide a sufficiently flexible bases to properly describe eigenfunctions with eigenvalues near the energy parameter E_l which is kept fixed. This scheme allows us to obtain all eigenvalues with a single diagonalization in contrast to APW methods.

Using the result of Theorem 3.2, it is only necessary for us to estimate the error introduced by linearization, say, the error made by using the radial function and its energy derivative from an energy parameter E_l other than at the eigenvalue $\hat{\lambda}_\delta$ found by APW method. This is done by assuming that the APW radial function $\chi_l(r, \hat{\lambda}_\delta)$ and the LAPW combination

$$\tilde{\chi}_l(r, E_l) = \alpha_l \chi_l(r, E_l) + \beta_l \dot{\chi}_l(r, E_l) \tag{3.43}$$

have the same logarithmic derivative with respect to r

$$\frac{\chi_l'(r, \hat{\lambda}_\delta)}{\chi_l(r, \hat{\lambda}_\delta)} = \frac{\tilde{\chi}_l'(r, E_l)}{\tilde{\chi}_l(r, E_l)} \tag{3.44}$$

at the spherical boundary, see [4, 33, 36]. Let $\sigma = |\hat{\lambda}_\delta - E_l|$. It has been analyzed in [4, 33] that under the assumption (3.44), the difference between $\tilde{\chi}_l(r, E_l)$ and the correct APW radial function $\chi_l(r, \hat{\lambda}_\delta)$ is of order σ^2, i.e.

$$\|\tilde{\chi}_l(r, E_l) - \chi_l(r, \lambda)\|_{H^1([0,R])} \sim \sigma^2.$$

Using similar arguments as that in the proof of Theorem 3.2, we obtain a priori error estimate of LAPW methods as

$$|\lambda - \lambda_\delta| \le C(K^{-(s-3/2)} + L^{-(s-3/2)} + \sigma^4), \tag{3.45}$$

$$\|u - u_\delta\|_\delta \le C(K^{-(s-3/2)} + L^{-(s-3/2)} + \sigma^2) \tag{3.46}$$

for any $s \in \mathbb{R}_+$.

Although the error of the eigenvalue approximations rely on the choice of the parameter E_l, the high order of this term results in that LAPW methods form a good bases set over a relatively large energy region. In most materials, it is quite adequate to choose E_l near the center of the bands of interest. However, in a few instances, there is no single choice of E_l that is adequate for all the bands that must be considered, then the energy region of interest may be divided into a few windows and separate computations should be carried out for each.

Remark 3.3. *The a priori error estimates* (3.45) *and* (3.46) *rely heavily on the assumption* (3.44)*, which is doubted in [29]. We can not prove this statement, nevertheless, the numerical experiments in Section 5 support the exponential convergence rates.*

In order to have enough variational flexibility in the radial bases functions, (L)APW+lo methods add new local bases to LAPW methods. The approximation space V_δ is spanned by $\{\omega_{\mathbf{k}}\}_{|\mathbf{k}|\le K}$ given by (3.42) and local orbitals $\{\varphi_i\}_{1\le i\le N}$ as

$$\varphi_i(\mathbf{r}) = \begin{cases} 0 & \text{in } \mathscr{D}, \\ \displaystyle\sum_{lm}^{L} [\alpha_{lm}\chi_{\varepsilon_i}(r, \varepsilon_i) + \beta_{lm}\dot{\chi}_{\varepsilon_i}(r, \varepsilon_i)] Y_{lm}(\theta, \phi) & \text{in } \mathscr{C}, \end{cases} \tag{3.47}$$

where the coefficients α_{lm} and β_{lm} do not depend on $\mathbf{k}$ but are determined by the requirement that φ_i is zero at the sphere boundary and normalized. Note that different energy parameter ε_i can be chosen so that different states can be described simultaneously. Note that $\tilde{B}_{NL} = \text{span}\{\varphi_i\}_{1\le i\le N}$ take place of the polynomial space in our nonconforming framework.

As shown by the numerical experiments in [35], APW+lo converges practically to identical results as the LAPW method, but allows significantly smaller bases sets (up to 50%) and thus reduce the computational cost drastically.

4 Error estimates for Kohn-Sham equations

We have given a priori error estimates for linear Schrödinger type eigenvalue problems in the previous section. In this section, we shall investigate the nonlinear KS equations (1.1), considering the convergence and a priori error estimates of the approximations obtained by the nonconforming method constructed in Section 3.1.

We shall introduce some notations first. For $\Bbbk \in \mathbb{R}^{N\times N}$, we denote its Frobenius norm by $|\Bbbk|$. We consider the functional space

$$\mathcal{H} \equiv (H^1_{\#}(\Omega))^N = \{(\phi_1, \phi_2, \cdots, \phi_N) : \ \phi_i \in H^1_{\#}(\Omega) \ (i = 1, 2, \cdots, N)\},$$

which is a Hilbert space associated with the induced norm $\|\cdot\|_{1,\Omega}$. In our discussion, we shall use the following spaces:

$$\mathcal{S}^{N\times N} = \{M \in \mathbb{R}^{N\times N} : M^T = M\}, \ \ \mathcal{A}^{N\times N} = \{M \in \mathbb{R}^{N\times N} : M^T = -M\},$$

and

$$\mathbb{Q} = \{\Phi \in \mathcal{H} : \langle \Phi^T \Phi\rangle = I^{N\times N}\} \quad \text{where} \quad \langle \Phi^T \Psi\rangle = \left(\int_\Omega \phi_i \psi_j\right)_{i,j=1}^N \in \mathbb{R}^{N\times N}.$$

For any $\Phi \in \mathcal{H}$, we may decompose $\mathcal{H}$ as a direct sum of three subspaces (see, e.g., [17, 34]):

$$\mathcal{H} = \mathcal{S}_\Phi \oplus \mathcal{A}_\Phi \oplus \mathcal{T}_\Phi, \tag{4.1}$$

where $\mathcal{S}_\Phi = \Phi\mathcal{S}^{N\times N}$, $\mathcal{A}_\Phi = \Phi\mathcal{A}^{N\times N}$, and $\mathcal{T}_\Phi = \left\{\Psi \in \mathcal{H} : \Psi^T\Phi = 0 \in \mathbb{R}^{N\times N}\right\}$.

For our nonconforming framework, we need $\mathcal{H}^\delta = (H^\delta_{\#}(\Omega))^N$ with the induced norm $\|\cdot\|_\delta$, and $\mathbb{Q}^\delta = \{\Phi \in \mathcal{H}^\delta : \langle \Phi^T\Phi\rangle = I^{N\times N}\}$. For any $\Phi \in \mathcal{H}^\delta$, the space $\mathcal{H}^\delta$ can be decomposed similarly as (4.1) into three subspaces

$$\mathcal{H}^\delta = \mathcal{S}^\delta_\Phi \oplus \mathcal{A}^\delta_\Phi \oplus \mathcal{T}^\delta_\Phi. \tag{4.2}$$

We also need the discrete space $\mathcal{V}_\delta = (V_\delta(\Omega))^N \subset \mathcal{H}^\delta$ with V_δ defined by (3.3).

Remark 4.1. *Following [17, 41], we can use Grassmann manifold to interpret the equivalence classes of orthonormal bases spanning the same N-dimensional subspace with respect to the unitary invariance. Under this framework, $\mathcal{T}^\delta_\Phi$ is the tangent space of the Grassmann manifold at Φ.*

4.1 Abstract Kohn-Sham model and nonconforming discretization

The ground state solutions of the KS equation for a molecular system can be obtained by minimizing the KS energy functional

$$E(\{\phi_i\}) = \frac{1}{2}\sum_{i=1}^{N}\int_\Omega |\nabla\phi_i(x)|^2 dx + \int_\Omega V_{ext}(x)\rho_\Phi(x)dx + \frac{1}{2}D(\rho_\Phi,\rho_\Phi) + \int_\Omega \mathcal{E}(\rho_\Phi(x))dx \qquad (4.3)$$

with respect to wavefunctions $\Phi = \{\phi_i\}_{i=1}^N \in \mathcal{H}$ under the orthogonality constraints $\langle \Phi^T\Phi\rangle = I^{N\times N}$. The function $\mathcal{E}(\rho)$ denotes the exchange-correlation energy per unit volume in an electron gas with density ρ and $\mathcal{E}'(t) = v_{xc}(t)$, and $D(\rho_\Phi,\rho_\Phi)$ denotes electron-electron coulomb energy

$$D(f,g) = \int_\Omega f(g * r^{-1}) = \int_\Omega\int_\Omega f(x)g(y)\frac{1}{|x-y|}dxdy.$$

The existence of a minimizer of the energy functional can be found in [1, 31]. The Euler-Lagrange equation associated with the minimization problem is

$$\begin{cases} (H_\Phi\phi_i, v) &= \big(\sum_{j=1}^{N}\lambda_{ij}\phi_j, v\big) \quad \forall\ v\in H^1_\#(\Omega), \quad i = 1,2,\cdots,N, \\ \int_\Omega \phi_i\phi_j &= \delta_{ij}, \end{cases} \qquad (4.4)$$

with H_Φ given by (1.2) and the Lagrange multiplier $\Lambda \equiv (\lambda_{ij})_{i,j=1}^N = \left(\int_\Omega \phi_j H_\Phi \phi_i\right)_{i,j=1}^N$. Note that (1.1) is obtained by diagonalization of the Lagrange multiplier since the energy functional and the Hamiltonian is invariant under any unitary transform of the KS orbitals, i.e., for any $\Phi\in\mathbb{Q}$,

$$E(\Phi) = E(\Phi U) \qquad \forall\ U = (u_{ij})_{i,j=1}^N \in \mathcal{O}^{N\times N}, \qquad (4.5)$$

where $\mathcal{O}^{N\times N}$ is the set of orthogonal matrices.

To obtain the a priori error estimates of the finite dimensional approximations, we shall represent KS equation in the following setting. Define

$$Y = \mathbb{R}^{N\times N}\times\mathcal{H}$$

with the associated norm $\|(\Lambda,\Phi)\|_Y = |\Lambda| + \|\Phi\|_{1,\Omega}$ for each $(\Lambda,\Phi)\in Y$. We may rewrite (4.4) as a nonlinear problem:

$$F((\Lambda,\Phi)) = 0 \in Y^*, \qquad (4.6)$$

where $F: Y\to Y^*$ is given by

$$\langle F((\Lambda,\Phi)),(\chi,\Gamma)\rangle = \sum_{i=1}^{N}\big(H_\Phi\phi_i - \sum_{j=1}^{N}\lambda_{ij}\phi_j,\gamma_i\big) + \sum_{i,j=1}^{N}\chi_{ij}\big(\int_\Omega\phi_i\phi_j - \delta_{ij}\big) \qquad (4.7)$$

with $\Gamma = (\gamma_1, \gamma_2, \cdots, \gamma_N) \in \mathcal{H}$ and $\mathbb{\chi} = (\chi_{ij})_{i,j=1}^N \in \mathbb{R}^{N\times N}$.

The Fréchet derivative of F at $(\Lambda, \Phi) : Y \to Y^*$ is defined by

$$\langle F'_{(\Lambda,\Phi)}((\mathbb{\mu}, \Psi)), (\mathbb{\chi}, \Gamma)\rangle = a_{(\Lambda,\Phi)}(\Psi, \Gamma) + \sum_{i,j=1}^N (\mu_{ij}\phi_j, \gamma_i) + \sum_{i,j=1}^N \chi_{ij} \int_\Omega (\psi_i\phi_j + \phi_i\psi_j) \tag{4.8}$$

for any $(\mathbb{\mu}, \Psi), (\mathbb{\chi}, \Gamma) \in Y$, where

$$\begin{aligned} a_{(\Lambda,\Phi)}(\Psi, \Gamma) &= \frac{1}{2}E''(\Phi)(\Psi, \Gamma) - \sum_{i,j=1}^N (\lambda_{ij}\psi_j, \gamma_i) \\ &= \sum_{i=1}^N \big(\frac{1}{2}(\nabla\psi_i, \nabla\gamma_i) + (V_{ext}\psi_i, \gamma_i) + (\mathcal{E}'(\rho_\Phi)\psi_i, \gamma_i) + D(\rho_\Phi, \psi_i\gamma_i) \\ &\quad -(\sum_{j=1}^N \lambda_{ij}\psi_j, \gamma_i) + \big(2\phi_i\mathcal{E}''(\rho_\Phi)\sum_{j=1}^N \phi_j\psi_j, \gamma_i\big) + \sum_{j=1}^N 2D(\phi_j\psi_j, \phi_i\gamma_i)\big) \end{aligned} \tag{4.9}$$

for $\Psi = (\psi_1, \psi_2, \cdots, \psi_N) \in \mathcal{H}$ and $\mathbb{\mu} = (\mu_{ij})_{i,j=1}^N \in \mathbb{R}^{N\times N}$.

We shall then address the nonconforming form of (4.6). Let

$$Y_\delta = \mathbb{R}^{N\times N} \times \mathcal{H}^\delta$$

with the associated norm $\|(\mathbb{\mu}, \Psi)\|_{Y_\delta} = |\mathbb{\mu}| + \|\Psi\|_\delta$ and $F_\delta : Y_\delta \to Y_\delta^*$ be an discrete operator defined by

$$\begin{aligned} \langle F_\delta((\Lambda_\delta, \Phi_\delta)), (\mathbb{\chi}_\delta, \Gamma_\delta)\rangle &= \frac{1}{2}\sum_{i=1}^N \big(\int_{\mathscr{C}} \nabla\phi_i\nabla\gamma_i + \int_{\mathscr{D}} \nabla\phi_i\nabla\gamma_i\big) + \sum_{i=1}^N \big((v_{ext} + v_H(\rho_\Phi) \\ +v_{xc}(\rho_\Phi))\phi_i, \gamma_i\big) - \sum_{i=1}^N \big(\sum_{j=1}^N \lambda_{ij}\phi_j, \gamma_i\big) + \sum_{i,j=1}^N \chi_{ij}\big(\int_\Omega \phi_i\phi_j - \delta_{ij}\big) \qquad \forall\ (\Lambda_\delta, \Phi_\delta), (\mathbb{\chi}_\delta, \Gamma_\delta) \in Y_\delta. \end{aligned}$$

We also denote the derivative of F_δ at $(\Lambda_\delta, \Phi_\delta) \in Y_\delta$ by $F'_{\delta,(\Lambda_\delta,\Phi_\delta)} : Y_\delta \to Y_\delta^*$ as

$$\begin{aligned} \langle F'_{\delta,(\Lambda_\delta,\Phi_\delta)}((\mathbb{\mu}_\delta, \Psi_\delta)), (\mathbb{\chi}_\delta, \Gamma_\delta)\rangle &= a^\delta_{(\Lambda_\delta,\Phi_\delta)}(\Psi_\delta, \Gamma_\delta) + \sum_{i,j=1}^N (\mu_{ij,\delta}\phi_{j,\delta}, \gamma_{i,\delta}) \\ &\quad + \sum_{i,j=1}^N \chi_{ij,\delta}\int_\Omega (\psi_{i,\delta}\phi_{j,\delta} + \phi_{i,\delta}\psi_{j,\delta}) \qquad \forall\ (\mathbb{\mu}_\delta, \Psi_\delta), (\mathbb{\chi}_\delta, \Gamma_\delta) \in Y_\delta, \end{aligned} \tag{4.10}$$

where $a^\delta_{(\Lambda_\delta,\Phi_\delta)}$ is given as (4.9) by replacing $(\nabla\psi_i, \nabla\gamma_i)$ with $\displaystyle\int_{\mathscr{C}} \nabla\psi_i\nabla\gamma_i + \int_{\mathscr{D}} \nabla\psi_i\nabla\gamma_i$.

For numerical discretization of (4.6), let

$$Y_n = \mathbb{R}^{N\times N} \times \mathcal{V}_\delta$$

and $F_n : Y_n \to Y_n^*$ be an nonconforming approximation of F defined by

$$\langle F_n((\Lambda_n, \Phi_n)), (\mathbb{X}_n, \Gamma_n)\rangle = \langle F_\delta((\Lambda_n, \Phi_n)), (\mathbb{X}_n, \Gamma_n)\rangle \quad \forall\ (\Lambda_n, \Phi_n), (\mathbb{X}_n, \Gamma_n) \in Y_n.$$

Then discretization of (4.6) by the nonconforming method can be written as

$$F_n((\Lambda_n, \Phi_n)) = 0 \in Y_n^*. \tag{4.11}$$

We also denote the derivative of F_n at $(\Lambda_n, \Phi_n) \in Y_n$ by $F'_{n,(\Lambda_n,\Phi_n)} : Y_n \to Y_n^*$ induced by (4.10).

Note that there are infinite number of solutions of (4.11) due to (4.5), we shall define

$$\mathbb{Q}^\Phi = \{\Psi \in \mathbb{Q}^\delta : \|\Psi - \Phi\|_{0,\Omega} = \min_{U\in\mathcal{O}^{N\times N}} \|\Psi U - \Phi\|_{0,\Omega}\}$$

for any $\Phi \in \mathbb{Q}$ to get rid of the redundancy. In our analysis, the following lemma will be used, whose proof can be referred to [12, 34].

Lemma 4.1. *If $\Phi \in \mathbb{Q}$, then $\Psi \in \mathbb{Q}^\Phi$ can be represented by*

$$\Psi = \Phi + \Phi S(W) + W,$$

where $W \in \mathcal{T}_\Phi^\delta$ and $S(W) \in \mathcal{S}^{N\times N}$.

4.2 A priori error estimates of the nonconforming approximations

Given $(\Lambda, \Phi) \in \mathcal{S}^{N\times N} \times \mathbb{Q}$, we define

$$X_\Phi = \mathcal{S}^{N\times N} \times (\mathcal{S}_\Phi^\delta \oplus \mathcal{T}_\Phi^\delta) \subset Y$$

with the induced norm $\|(\mathbb{\mu}, \Psi)\|_{X_\Phi} = |\mathbb{\mu}| + \|\Psi\|_\delta$ for each $(\mathbb{\mu}, \Psi) \in X_\Phi$ and

$$X_{\Phi,n} = \mathcal{S}^{N\times N} \times (\mathcal{V}_\delta \cap (\mathcal{S}_\Phi^\delta \oplus \mathcal{T}_\Phi^\delta)).$$

We assume here and hereafter that $y_0 \equiv (\Lambda_0, \Phi_0)$ is a ground state solution of (4.4), where $\Lambda_0 = (\lambda_{0,ij})_{i,j=1}^N$ and $\Phi_0 = (\phi_{0,1}, \phi_{0,2}, \cdots, \phi_{0,N})$. We shall derive the existence of a unique local discrete solution $y_n \in X_{\Phi_0,n}$ of (4.11) in the neighborhood of y_0 and further obtain the a priori error estimate.

The analysis of finite dimensional approximations will be carried out under the following two assumptions:

A1 There exists a constant $\alpha \in (0, 1]$ such that $|\mathcal{E}''(t)| + |t\mathcal{E}'''(t)| \lesssim 1 + t^{\alpha-1} \quad \forall\ t > 0$.

A2 There exists a positive constant γ depending on (Λ_0, Φ_0) such that

$$a^\delta_{(\Lambda_0,\Phi_0)}(\Psi, \Psi) \geq \gamma\|\Psi\|_\delta^2 \quad \forall\ \Psi \in \mathcal{T}^\delta_{\Phi_0}. \tag{4.12}$$

Remark 4.2. *We see that for a symmetric bilinear form $\tilde{a}(u, v) = (Au, v)$ Assumption* **A2** *is true for $\tilde{a}(\cdot, \cdot)$ if the operator A has N lowest eigenvalues $\lambda_1, \cdots, \lambda_N$ and there is a gap between the lowest Nth eigenvalue and the $(N + 1)$th eigenvalue [12, 41].*

Remark 4.3. *Under the framework of Grassmann manifold [17, 41], Assumption* **A2** *can be viewed as imposing the elliptic condition on* $a^{\delta}_{(\Lambda_0,\Phi_0)}(\cdot,\cdot)$ *on the tangent space.*

The following lemma will be used in our analysis, which can be proved under the assumption **A1** by using the same arguments as that in [12, Lemma 4.6] and [14, Lemma 2.1].

Lemma 4.2. *Let* $y_1 = (\Lambda_1, \Phi_1)$ *and* $y_2 = (\Lambda_2, \Phi_2) \in Y_\delta$ *satisfy* $\|y_1\|_{Y_\delta} + \|y_2\|_{Y_\delta} \le \bar{C}$. *If the assumption* **A1** *is satisfied, then there exists a constant* C_F *depending on* $\bar{C}$ *such that*

$$\|F_\delta(y_1) - F_\delta(y_2)\|_{Y_\delta^*} \le C_F \|y_1 - y_2\|_{Y_\delta} \quad \forall\ y_1, y_2 \in Y_\delta. \tag{4.13}$$

Moreover, if Assumption **A2** *is satisfied, then there is a constant* C'_F *such that*

$$\|F'_{\delta,y_1} - F'_{\delta,y_2}\|_{Y_\delta^*} \le C'_F(\|y_1 - y_2\|^{\alpha}_{Y_\delta} + \|y_1 - y_2\|^2_{Y_\delta}) \quad \forall\ y_1, y_2 \in Y_\delta. \tag{4.14}$$

Under the assumption **A2**, we have

Lemma 4.3. *If the assumption* **A2** *is satisfied, then* $F'_{\delta,y_0} : X_{\Phi_0} \to X^*_{\Phi_0}$ *is an isomorphism.*

Proof. It is sufficient to prove that equation

$$F'_{\delta,y_0}((\mathbb{\mu}, \Psi)) = (\mathbb{\eta}, g) \tag{4.15}$$

is uniquely solvable in X_{Φ_0} for every $(\mathbb{\eta}, g) \in X^*_{\Phi_0}$. To this end we define the following bilinear forms $a_{\Phi_0} : \mathcal{H}^\delta \times \mathcal{H}^\delta \to \mathbb{R}$ and $b_{\Phi_0}, c_{\Phi_0} : \mathcal{H}^\delta \times \mathbb{R}^{N\times N} \to \mathbb{R}$ by

$$\begin{aligned}
a_{\Phi_0}(\Psi, \Gamma) &= a^{\delta}_{(\Lambda_0,\Phi_0)}(\Psi, \Gamma),\\
b_{\Phi_0}(\Psi, \mathbb{\chi}) &= \sum_{i,j=1}^{N} \chi_{ij}(\phi_{0,i}, \psi_j),\\
c_{\Phi_0}(\Psi, \mathbb{\chi}) &= \sum_{i,j=1}^{N} \chi_{ij}\big((\phi_{0,i}, \psi_j) + (\phi_{0,j}, \psi_i)\big).
\end{aligned}$$

Using (4.8), we may rewrite (4.15) as follows: find $\mathbb{\mu} \in \mathcal{S}^{N\times N}$ and $\Psi \in \mathcal{S}^\delta_{\Phi_0} \oplus \mathcal{T}^\delta_{\Phi_0}$ such that

$$\begin{cases}
a_{\Phi_0}(\Psi, \Gamma) + b_{\Phi_0}(\Gamma, \mathbb{\mu}) = (g, \Gamma) & \forall\ \Gamma \in \mathcal{S}^\delta_{\Phi_0} \oplus \mathcal{T}^\delta_{\Phi_0},\\
c_{\Phi_0}(\Psi, \mathbb{\chi}) = \sum_{i,j=1}^{N} \chi_{ij}\eta_{ij} & \forall\ \mathbb{\chi} \in \mathcal{S}^{N\times N}.
\end{cases} \tag{4.16}$$

For any given $\mathbb{\chi} \in \mathcal{S}^{N\times N}$, we can choose $\Psi = \Phi_0\mathbb{\chi}$, and thus

$$c_{\Phi_0}(\Psi, \mathbb{\chi}) = 2\sum_{i,j=1}^{N} |\chi_{ij}|^2, \tag{4.17}$$

where $\langle \Phi_0^T \Phi_0 \rangle = I^{N\times N}$ is used. Note that a simple calculation leads to

$$\|\Psi\|_\delta = \|\Phi_0 \chi\|_{1,\Omega} \lesssim (\sum_{i,j=1}^{N} |\chi_{ij}|^2)^{1/2} \|\Phi_0\|_{1,\Omega}. \tag{4.18}$$

By taking into account (4.17), (4.18) and the fact that $\|\Phi_0\|_{1,\Omega} \le C$, we obtain

$$\inf_{\chi\in\mathcal{S}^{N\times N}} \sup_{\Psi\in\mathcal{S}^\delta_{\Phi_0}} \frac{c_{\Phi_0}(\Psi,\chi)}{\|\Psi\|_\delta (\sum_{i,j=1}^{N} |\chi_{ij}|^2)^{1/2}} \ \ge\ \kappa_c, \tag{4.19}$$

where $\kappa_c > 0$ is independent of χ. Hence, there exists a unique solution $\Psi_S \in \mathcal{S}^\delta_{\Phi_0}$ such that

$$c_{\Phi_0}(\Psi_S,\chi) = \sum_{i,j=1}^{N} \chi_{ij}\eta_{ij} \quad \forall\ \chi \in \mathcal{S}^{N\times N}.$$

Therefore (4.16) is equivalent to: find $\Psi_0 \in \mathcal{T}^\delta_{\Phi_0}$ such that

$$a_{\Phi_0}(\Psi_0,\Gamma) = (g,\Gamma) - a_{\Phi_0}(\Psi_S,\Gamma) \quad \forall\ \Gamma \in \mathcal{T}^\delta_{\Phi_0}. \tag{4.20}$$

The unique solvability of (4.20) is a direct consequence of (4.12).

Using similar arguments to that from (4.17) to (4.19), we get

$$\inf_{\chi\in\mathcal{S}^{N\times N}} \sup_{\Psi\in\mathcal{S}^\delta_{\Phi_0}} \frac{b_{\Phi_0}(\Psi,\chi)}{\|\Psi\|_\delta (\sum_{i,j=1}^{N} |\chi_{ij}|^2)^{1/2}} \ \ge\ \kappa_b,$$

where $\kappa_b > 0$ is independent of χ. This implies that equation

$$b_{\Phi_0}(\Gamma,\mu) = (g,\Gamma) - a_{\Phi_0}(\Psi_0+\Psi_S,\Gamma) \quad \forall\ \Gamma \in \mathcal{S}^\delta_{\Phi_0}$$

has a unique solution $\mu_S \in \mathcal{S}^{N\times N}$.

We have proved that for any $(\eta, g) \in X^*_{\Phi_0}$ in (4.16), there exists a unique solution $(\mu_S, \Psi_0 + \Psi_S)$. This indicates that F'_{δ,y_0} is an isomorphism from X_{Φ_0} to $X^*_{\Phi_0}$ and completes the proof. □

Before giving a discrete counterpart of Lemma 4.3, we shall introduce two projections. First, we define the projection $\tilde{\Pi}_n : \mathbb{Q} \to \mathcal{V}_\delta \cap \mathbb{Q}$ such that

$$\|\tilde{\Pi}_n \Phi - \Phi\|_\delta = \min_{\Psi\in\mathcal{V}_\delta\cap\mathbb{Q}} \|\Psi - \Phi\|_\delta \quad \forall\ \Phi \in \mathbb{Q}.$$

To project further into $X_{\Phi,n}$, we then define $\Pi_n : \mathcal{S}^{N\times N} \times \mathbb{Q} \to X_{\Phi,n}$ by

$$\Pi_n(\Lambda,\Phi) = (\Lambda, (\tilde{\Pi}_n\Phi)\tilde{U}) \qquad \forall\ (\Lambda,\Phi) \in \mathcal{S}^{N\times N} \times \mathbb{Q},$$

where

$$\tilde{U} = \arg \min_{U\in\mathcal{O}^{N\times N}} \|(\tilde{\Pi}_n\Phi)U - \Phi\|_{0,\Omega}.$$

From Lemma 4.1, we see that $\Pi_n : \mathcal{S}^{N\times N} \times \mathbb{Q} \to X_{\Phi,n}$ is well-defined. We obtain by a direct estimate (see [14, proof of Lemma 3.3]) that for $y = (\Lambda, \Phi) \in \mathcal{S}^{N\times N} \times \mathbb{Q}$,

$$\|\Pi_n y - y\|_{X_\Phi} \lesssim \inf_{\Psi\in\mathcal{V}_\delta} \|\Psi - \Phi\|_\delta. \tag{4.21}$$

Note that $F'_{\delta,y_0} : X_{\Phi_0} \to X^*_{\Phi_0}$ being an isomorphism is equivalent to the following inf-sup condition

$$\inf_{y_1\in X_{\Phi_0}} \sup_{y_2\in X_{\Phi_0}} \frac{\langle F'_{\delta,y_0} y_1, y_2\rangle}{\|y_1\|_{X_{\Phi_0}} \|y_2\|_{X_{\Phi_0}}} = \beta > 0 \tag{4.22}$$

with the constant satisfying $\beta^{-1} = \|F'^{-1}_{y_0}\|$. We can derive from (4.21) and a direct calculation (see, e.g. [14]) that

$$\inf_{y_1\in X_{\Phi_0,n}} \sup_{y_2\in X_{\Phi_0,n}} \frac{\langle F'_{\delta,y_0} y_1, y_2\rangle}{\|y_1\|_{X_{\Phi_0}} \|y_2\|_{X_{\Phi_0}}} \geq \frac{\beta}{2},$$

which together with the fact that F'_n satisfies the Hölder condition analogous to (4.14)

$$\|F'_{n,y_0} - F'_{n,\Pi_n y_0}\| \lesssim \|y_0 - \Pi_n y_0\|^\alpha_{X_{\Phi_0}} + \|y_0 - \Pi_n y_0\|^2_{X_{\Phi_0}}$$

leads to the following discrete counterpart of Lemma 4.3.

Lemma 4.4. *If the assumption* **A1** *and* **A2** *are satisfied, then there exists $n_0 \in \mathbb{Z}_+$ such that $F'_{n,\Pi_n y_0} : X_{\Phi_0,n} \to X^*_{\Phi_0,n}$ is an isomorphism for all $\varrho \geq n_0$. Moreover, there is a constant $M > 0$ such that*

$$\|F'^{-1}_{n,\Pi_n y_0}\| \leq M \quad \forall\ \varrho \geq n_0.$$

Now we have the main result of this section as follows.

Theorem 4.1. *If the assumptions* **A1** *and* **A2** *are satisfied, then there exist $\sigma > 0$, $n_1 \in \mathbb{Z}_+$ such that* (4.11) *has a unique local solution $y_n = (\Lambda_n, \Phi_n) \in X_{\Phi_0,n} \cap B_\sigma(y_0)$ for all $\varrho \geq n_1$.*

Moreover, we have the error estimate for y_n as

$$|\Lambda_0 - \Lambda_n| + \|\Phi_0 - \Phi_n\|_\delta \leq C\varrho^{-(s-3/2)} \quad \forall\ s \in \mathbb{R}_+. \tag{4.23}$$

Proof. The idea of this proof is to construct a contractive mapping whose fixed point is y_n. We rewrite (4.11) as

$$F_n(y_n) - F_n(\Pi_n y_0) = -F_n(\Pi_n y_0). \tag{4.24}$$

Using (4.13), we have

$$\begin{aligned}
\|F_n(\Pi_n y_0)\|_{X^*_{\Phi_0,n}} &= \|F_n(\Pi_n y_0) - F_n(y_0)\|_{X^*_{\Phi_0,n}} + \|F_n(y_0)\|_{X^*_{\Phi_0,n}} \\
&\leq \|F_\delta(\Pi_n y_0) - F_\delta(y_0)\|_{X^*_{\Phi_0}} + \sup_{(\chi_n,\Gamma_n)\in X_{\Phi_0,n}} \frac{\langle F_\delta((\Lambda_0,\Phi_0)), (\chi_n,\Gamma_n)\rangle}{\|(\chi_n,\Gamma_n)\|_{X^*_{\Phi_0}}} \\
&\lesssim \|y_0 - \Pi_n y_0\|_{X_{\Phi_0}} + L^{-(s-1)}\|\Phi_0\|_{H^s(\mathscr{D})}.
\end{aligned}$$

From (4.24) and Lemma 4.4, we may define the map $\mathcal{N} : B_R(\Pi_n y_0) \cap X_{\Phi_0,n} \to X_{\Phi_0,n}$ by

$$F'_{n,\Pi_n y_0}(\mathcal{N}(x) - \Pi_n y_0) = -F_n(\Pi_n y_0) - (x - \Pi_n y_0) \int_0^1 \big(F'_{n,\Pi_n y_0 + t(x-\Pi_n y_0)} - F'_{n,\Pi_n y_0}\big) dt \quad (4.25)$$

when $\varrho \geq n_0$.

We will show that $\mathcal{N}$ is a contraction from $B_R(\Pi_n y_0) \cap X_{\Phi_0,n}$ into $B_R(\Pi_n y_0) \cap X_{\Phi_0,n}$ if R is chosen sufficiently small and ϱ is large enough.

First, we prove that $\mathcal{N}$ maps $B_R(\Pi_n y_0) \cap X_{\Phi_0,n}$ to $B_R(\Pi_n y_0) \cap X_{\Phi_0,n}$ for sufficiently small R. Note that $F'_{n,\Pi_n y_0}$ is an isomorphism on $X_{\Phi_0,n}$ if ϱ is sufficiently large. For each $x \in B_R(\Pi_n y_0)$, we have $\mathcal{N}(x) - \Pi_n y_0 \in X_{\Phi_0,n}$ and

$$\begin{aligned} & \|\mathcal{N}(x) - \Pi_n y_0\|_{X_{\Phi_0}} \\ \leq\ & M\big(\|F_n(\Pi_n y_0)\|_{X^*_{\Phi_0,n}} + R \int_0^1 \|F'_{n,\Pi_n y_0 + t(x-\Pi_n y_0)} - F'_{n,\Pi_n y_0}\| dt\big) \\ \leq\ & CM\big(\|\Pi_n y_0 - y_0\|_{X_{\Phi_0}} + R(R^\alpha + R^2) + L^{-(s-1)}\|\Phi_0\|_{H^s(\mathscr{D})}\big). \end{aligned}$$

Since $CM(\|\Pi_n y_0 - y_0\|_{X_{\Phi_0}} + R^{1+\alpha} + R^3 + L^{-(s-1)}\|\Phi_0\|_{H^s(\mathscr{D})})$ can be estimated by R when R is sufficiently small and ϱ is sufficiently large, we have that $\mathcal{N}(x) \in B_R(\Pi_n y_0)$. It is clear that R can be chosen independently of ϱ.

Next, we show that $\mathcal{N}$ is a contraction on $B_R(\Pi_n y_0) \cap X_{\Phi_0,n}$. If $x_1, x_2 \in B_R(\Pi_n y_0) \cap X_{\Phi_0,n}$, then

$$F'_{n,\Pi_n y_0}(\mathcal{N}(x_1) - \mathcal{N}(x_2)) = (x_1 - x_2) \int_0^1 \big(F'_{n,\Pi_n y_0} - F'_{n,x_1 + t(x_2 - x_1)}\big) dt.$$

Thus, $\|\mathcal{N}(x_1) - \mathcal{N}(x_2)\|_{X_{\Phi_0}}$ can be estimated from (4.14) as

$$\begin{aligned} & \|\mathcal{N}(x_1) - \mathcal{N}(x_2)\|_{X_{\Phi_0}} \\ \leq\ & M\|x_2 - x_1\|_{X_{\Phi_0}} \int_0^1 \big\|F'_{n,\Pi_n y_0} - F'_{n,x_1 + t(x_2 - x_1)}\big\| dt \\ \leq\ & CM(R^\alpha + R^2)\|x_1 - x_2\|_{X_{\Phi_0}}. \end{aligned}$$

We obtain for sufficiently small R that $CM(R^\alpha + R^2) < 1$ and hence $\mathcal{N}$ is a contraction on $B_R(\Pi_n y_0)$.

We are now able to use Banach's Fixed Point Theorem to obtain the existence and uniqueness of a fixed point y_n of map $\mathcal{N} : B_R(\Pi_n y_0) \cap X_{\Phi_0,n} \to B_R(\Pi_n y_0) \cap X_{\Phi_0,n}$, which is the solution of $F_n(y_n) = 0$.

Take $x = y_n$ in (4.25), we have

$$\begin{aligned} \|y_n - \Pi_n y_0\|_{X_{\Phi_0}} \ \lesssim\ & \|y_0 - \Pi_n y_0\|_{X_{\Phi_0}} + L^{-(s-1)}\|\Phi_0\|_{H^s(\mathscr{D})} \\ & + \|y_n - \Pi_n y_0\|_{X_{\Phi_0}} (\|y_n - \Pi_n y_0\|^\alpha_{X_{\Phi_0}} + \|y_n - \Pi_n y_0\|^2_{X_{\Phi_0}}), \end{aligned}$$

which together with the fact that $\|y_n - \Pi_n y_0\|_{X_{\Phi_0}}$ can be arbitrary small implies

$$\|y_n - \Pi_n y_0\|_{X_{\Phi_0}} \lesssim \|y_0 - \Pi_n y_0\|_{X_{\Phi_0}} + L^{-(s-1)}\|\Phi_0\|_{H^s(\mathscr{D})}. \quad (4.26)$$

Using Lemma 2.1, Lemma 3.1, (4.21), (4.26), and the trigonal inequality

$$\|y_n - y_0\|_{X_{\Phi_0}} \leq \|y_n - \Pi_n y_0\|_{X_{\Phi_0}} + \|y_0 - \Pi_n y_0\|_{X_{\Phi_0}},$$

we can obtain (4.23). This completes the proof. □

Remark 4.4. *The arguments in this section are related to the techniques in [14, 30, 48]. We shall point out that [14, 30] are also devoted to DFT models, nevertheless, the theory in [14] can not be applied to nonconforming methods, and [30] analyze the orbital-free DFT model which consider the lowest eigenvalue only.*

5 Numerical experiments

We shall test our theoretical results by some numerical experiments. Since the analytical solutions of the eigenvalue problem are not available, we use the numerical solutions on the finest discretization for references to calculate the approximation errors.

Example 1. Solve the linear eigenvalue problem: Find $\lambda \in \mathbb{R}$ and $u \in H^1_{\#}(\Omega)$ such that

$$-\frac{1}{2}\Delta u + V_{ext} u = \lambda u,$$

where $\Omega = [-5, 5]^3$ and the external potential $V_{ext}(r) = -\frac{1}{r} - \frac{1}{2r_0 - r}$ for $r < r_0$ and $V_{ext}(r) = -2/r_0$ for $r \geq r_0$. Note that the periodic potential V_{ext} is sufficiently smooth expect for the nuclei positions, so the eigenfunction u is asymptotically well behaved due to Lemma 2.1.

We compare the numerical errors of plane wave method and our nonconforming method in Figure 5.3. It is shown that the convergence rate is improved by the nonconforming discretization, which support the theoretical results in this paper. The numerical errors obtained by different choices of atomic spheres are presented in Figure 5.4. We observe not only the exponential convergence rate of the nonconforming approximations but also a faster rate with larger spheres, since the eigenfunctions in the smaller interstitial region are more smooth and propitious to plane wave methods. The eigenfunctions on x-axis is displayed in Figure 5.5, from which we observe that the augmented methods can catch the cusp at the nuclear position while the plane wave methods can not.

We also present the numerical errors with respect to the order of radial polynomial bases in Figure 5.6. We observe that given a sufficiently large K, the errors of eigenvalue approximations converge exponentially.

Example 2. We consider a hydrogen atom by APW method. The atom is computed with a periodic boundary condition with the supercell $\Omega = [-5, 5]^3$.

Since the APW bases is energy dependent which lead to nonlinear equations, the eigenvalues are normally solved by the "root tracing" technique which determine the eigenvalues by varying the energy parameter ε numerically to satisfy the condition

$$\det(H_\varepsilon - \varepsilon M_\varepsilon) = 0,$$

where H_ε and M_ε are Hamilton matrix and mass matrix generated by bases $\omega^\varepsilon_{\mathbf{k}}$ given in (3.29). Instead of calculating the determinant of $H_\varepsilon - \varepsilon M_\varepsilon$ (which varies strongly and is difficult for

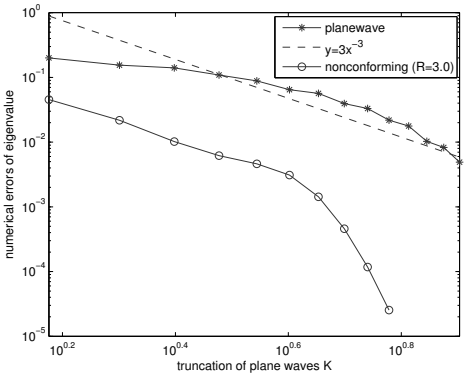

Figure 5.3: Numerical errors of planewave method and nonconforming method.

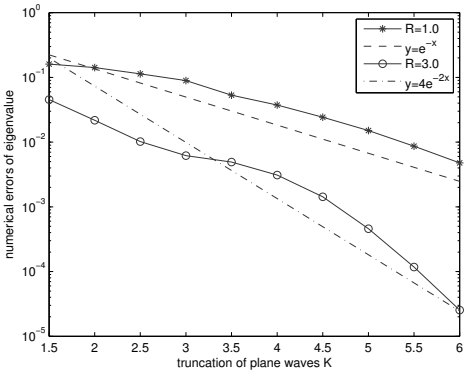

Figure 5.4: Numerical errors of nonconforming method with different spherical radius.

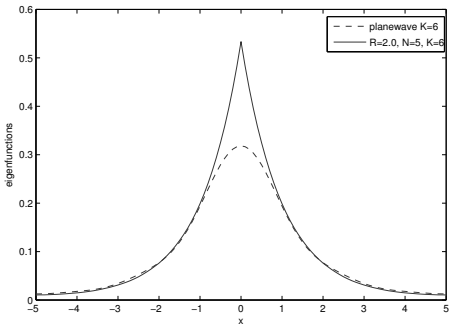

Figure 5.5: Radial wavefunctions obtained by plane waves and nonconforming methods.

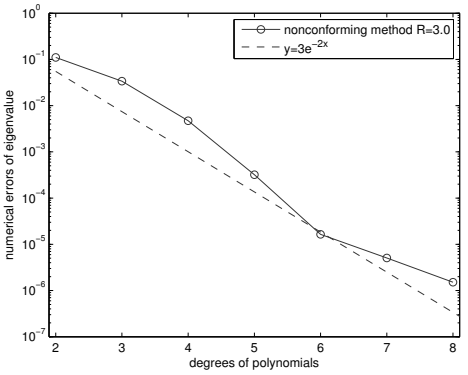

Figure 5.6: Numerical errors of the nonconforming approximations with respect to the order of polynomials radial bases with fixed $K = 6$.

root interpolation), we here compute the eigenvalue λ_ε of $M_\varepsilon^{-1} H_\varepsilon$ for each parameter ε, then calculate the difference between the eigenvalue and the parameter, say $\lambda_\varepsilon - \varepsilon$. The eigenvalues of the nonlinear problem can be found where the difference is 0 by interpolation (see, Figure 5.7). The numerical errors of plane wave method and APW method are compared in Figure 5.8, from which we observe that the APW method is much more accurate.

We shall mention that the computational cost of this nonlinear problem is extremely huge even for medium size systems. In contrast, LAPW(+lo) bases can result in straightforward linear eigenvalue problems and reduce the computational cost significantly.

Example 3. To examine the performance of LAPW approximations, we use the package Exciting [50] to calculate the aluminium (Al) and lithium-fluorine (LiF) crystals. Excting is a full-potential all-electron DFT package based on the LAPW+lo methods and use a self-consistent field iteration for the nonlinear KS equations. The convergence of the numerical errors are presented in Figure 5.9, which shows exponential convergence of the ground state

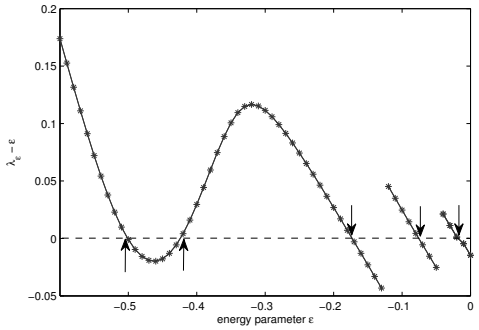

Figure 5.7: Search for the eigenvalues of the nonlinear problem generated by APW bases.

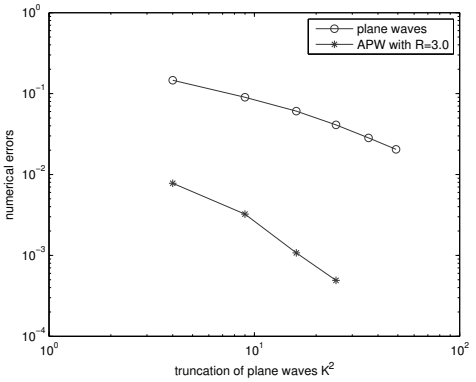

Figure 5.8: Numerical errors of the plane wave method and APW method.

energy approximations.

Moreover, we compare the full-potential computations using package Excting and the pseudopotential computations using package Abinit [24, 49] for the LiF crystal. The numerical results are presented in atomic units (a.u.). In Figure 5.10, we plot the ground state energy as a function of the lattice constant for LiF crystal using different packages and estimate the optimal lattice constant. The same plane wave truncation are used for both methods, say, $K = 12$. We observe that the optimal lattice constant obtained by LAPW method is closer to the experimental value 7.61 a.u. than the plane wave computations, which illustrate the necessity of the LAPW full-potential calculations. We also plot in Figure 5.11 the electron densities on a plane (the structure is presented in the left of the figure) obtained by these two methods, from which we see that the true density including the core electrons is obtained by full-potential calculations, whereas the pseudopotential calculations can only have a vague density of valence electrons.

6 Concluding remarks

In this paper, we analyze the augmented plane wave methods which are widely used in full-potential electronic structure calculations. We introduce a nonconforming method and the augmented plane wave methods are viewed as a modified scheme. We obtain a priori error estimates of the nonconforming method for both linear Schrödinger equations and nonlinear KS equations, and present some numerical results to support our theory. Instead of polynomials, more physical bases using Gaussian or Slater type bases functions around the nuclei may be incorporated in this nonconforming framework. However, the difficulties lie in that all χ_is do not vanish at the spherical surface, which may generate too many bases functions in computations. The discontinuous Galerkin (DG) methods may be a proper way to handel this problem, in which different areas can be approximated by completely sperate bases and matched together by DG schemes [15].

Similar to APW method, the Muffin-tin orbital (MTO) approach [2, 4, 36] is another type

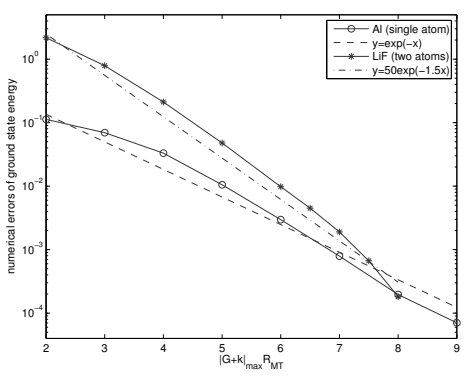

Figure 5.9: Numerical errors of the ground state energy for Al and LiF by the exciting code using LAPW+lo bases.

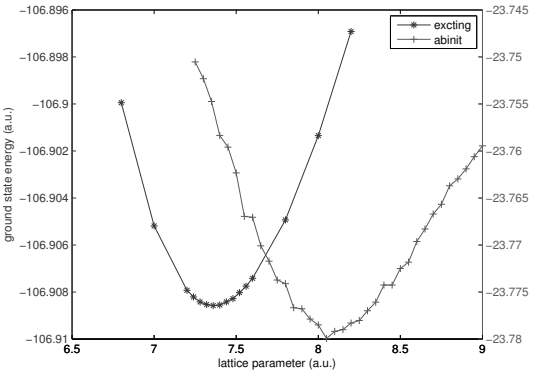

Figure 5.10: Computing the lattice constant of LiF using packages Exciting (y-axis on the left) and Abinit (y-axis on the right).

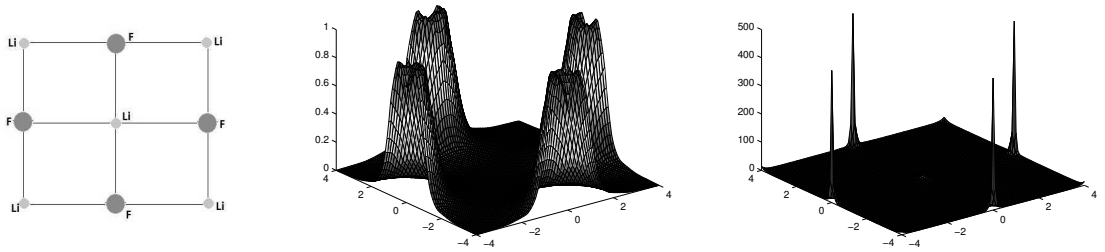

Figure 5.11: Electron density of LiF obtained by the packages Exciting and Abinit. Left: the structure of the plane. Middle: result of Abinit. Right: result of Excting.

of atomic sphere methods, which exploits the same idea that divides the electronic structure problem and provides efficient representation of atomic-like features that are rapidly varying near each nucleus and smoothly varying functions between the atoms respectively. The MTO method reformulates the multiple-scattering (MST, also called KKR since it is invented independently by Korringa, Kohn and Rostoker [36]) methods, and lead to physically meaningful descriptions of the electronic bands in terms of a small bases of localized, augmented functions.

The MTO bases are defined as the following functions that depend separately on κ and ε,

$$\omega_{lm}^{MTO} = i^l Y_{lm} \begin{cases} \chi_l(r,\varepsilon) + \kappa \cot(\eta_l(\varepsilon)) j_l(\kappa r) & \text{in } \mathscr{C}, \\ \kappa n_l(\kappa r) & \text{in } \mathscr{D}, \end{cases} \tag{6.1}$$

where χ_l is the solution of (3.28), j_l and n_l are spherical Bessel and Neumann functions respectively (for negative energies, the Neumann functions are replaced by Hankel functions), and η_l is determined by requiring that the bases functions match the value and slope at the spherical boundary. The equations for many atoms can be derived using an expansion theorem

and the tail cancelation condition, which expresses the tail of an MTO extending into another sphere in terms of functions centered on that sphere (see, e.g. [2, 36]). This amounts to a transformation of the KKR method and (the energy dependent bases) would lead to nonlinear eigenvalue equations. Since the solutions obtained by MTO methods satisfy the equation both inside and outside the spheres, the convergence of the MTO approximations can be proven using similar arguments as that in this paper (the detail proof will be addressed elsewhere), and the error is only determined by the truncation of angular momentum L.

For linearized Muffin-tin orbital (LMTO) methods, the error estimates is far too difficult compared with LAPW methods. For LAPW methods, it is only necessary for us to estimate the error introduced by linearization and the numerical integration of plane waves in the interstitial region can be done quite accurately. However, the expressions for the matrix elements in the interstitial region for LMTO methods are much more complicated, which apply atomic sphere approximation (ASA) and use the space-filling cells (Wigner-Seitz cells, see, e.g. [4, 36]) neglecting the interstitial region. These error analysis shall be investigated in our future works.

Acknowledgement

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